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FINAL REPORT

Project Title: The Development of High Transition Temperature
Superconducting Ceramic Thick Films and Wire Composites.

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Co-principal Investigators:

Dr. Jack E. Crow, Department of Materials Research and Technology, Florida
State University, Tallahassee, FL 32306

Dr. Sidney Stein, Electro-Science Laboratories Inc. P.O. Box 1059, 416E. Church
Road, King of Prussia, PA 19406

Dr. Richard Wahlers, Electro-Science Laboratories Inc. P.O. Box 059, 416E.
Church Road, King of Prussia, PA 19406

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I). Introduction and Description of Scientific Goals

This project is directed at establishing the relevant materials and processing parameters related to the application of high transition temperature oxide superconductors to thick film ceramic microelectronics and the development of superconducting ceramic tapes and wire composites.

II). Material and Powder Synthesis

The availability of a reliable technique for producing large quantities of phase pure, submicron powders is a critical prerequisite to thick film development and many other ceramic processing areas. The synthesis work carried out in response to this requirement has been supported by the DARPA/ONR contract and leveraged funds provided by the Commonwealth of Pennsylvania. This effort has focused on the areas listed below.

- A) The application and refinement of freeze drying technology to the production of high temperature superconducting powders, with particular emphasis on $\text{YBa}_2\text{Cu}_3\text{O}_7$.
- B) The use of liquid ammonia as a solvent for nitrate and acetate precursors of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ system and the fundamental issues of the chemistry involved.
- C) The application and refinement of gel technology to the production of phase pure, sub-micron precursors of $\text{YBa}_2\text{Cu}_3\text{O}_7$.
- D) The preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ from fused hydroxides.
- E) The preparation of impurity doped high T_c samples to aid in the understanding of flux pinning and enhancement mechanisms leading to higher critical temperatures.

A) Freeze Dried Fabrication of Powders.

The widespread use of freeze drying technology in the ceramic industry makes it a logical methodology for use in the production of high temperature superconducting powders. Freeze drying is employed to ensure the optimum mixing of the constituent elements. If a system consists of a number of solutes dissolved in a solvent, instantaneous freezing of the solvent ensures that the solutes remain in the same distribution as that found in the solution state. Subsequent removal of the now frozen solvent by sublimation results in a solid composed of a random mixture of the solutes, eliminating the need in the case of

the superconducting ceramics of the lengthy and labour intensive grinding and regrinding preparation step. The technical problems associated with achieving this desired result are numerous and are discussed in length in the Ph.D thesis entitled Synthesis and Characterization of High Temperature Superconductors Nicholas V. Coppa accompanying this report and partially funded by this contract. An abbreviated discussion is given below.

An important consideration in the preparation of aqueous solutions of the Yttrium, Barium and Copper nitrates employed is the high precision measurement of the waters of hydration, as these can vary considerably from the suppliers values. A solution of the various ions having a molar ratio of 1:2:3 for Y:Ba:Cu was prepared, with an absolute concentration for the Yttrium ion of $\leq 0.05\text{M}$. The filtered, degassed liquid was fed simultaneously into an ultrasonic atomizer (5W Sonotek) at a rate of 1 l/hour producing a fine spray of $\sim 10\text{ }\mu\text{m}$ droplets. The nozzle of the atomizer was position $\sim 2.5\text{ cm}$ above the surface of a stirred liquid nitrogen bath causing the spray to freeze and settle into the bath as a fine blue 'snow'. This was collected and placed in a commercial Dura-Top/Dry freeze drying system operating at a temperature of $\sim -40\text{ }^\circ\text{C}$ and pressure $< 30\text{ }\mu\text{m Hg}$ for a period typically of order 3 days for a 100g batch. The resultant green-blue powder was stored under dry nitrogen.

Over 100 samples of this precursor were subjected to various heat treatment schedules in order to optimize the yield of superconductor. Close observation of this treatment allowed 4 separate stages of processing to be identified; dehydration, denitration, reaction and oxygenation.

Dehydration of the material was deemed necessary by the observation of a phase melting due to the re-resolution of the precursor by the water of hydration released and subsequently trapped in the interstitial voids of the material. Typically dehydration consisted of heating the material at $0.3\text{ }^\circ\text{C/min}$ to $90\text{ }^\circ\text{C}$, holding for 9-12 hours and then increasing the temperature to $160\text{ }^\circ\text{C}$ under continuous vacuum.

Denitration of the precursor was achieved by plunging the sample into a $600\text{ }^\circ\text{C}$ furnace in flowing oxygen and holding for approximately 2 hours.

The precursor either in powder or pressed pellet form was reacted by heating to $925\text{ }^\circ\text{C}$ under flowing oxygen at a rate of $7\text{ }^\circ\text{C/min}$ with a hold time at this temperature of 2 hours. The sample was oxygenated by lowering the temperature to $520\text{ }^\circ\text{C}$ at $3\text{ }^\circ\text{C/min}$ and holding for 2 hours before cooling to room temperature.

Analysis and characterization of the material both before and after heat treatment was accomplished using a variety of methods including Xray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Resistivity measurements were made to determine the transition temperature and magnetization to determine the superconducting fraction. The results of these experiments showed that the freeze

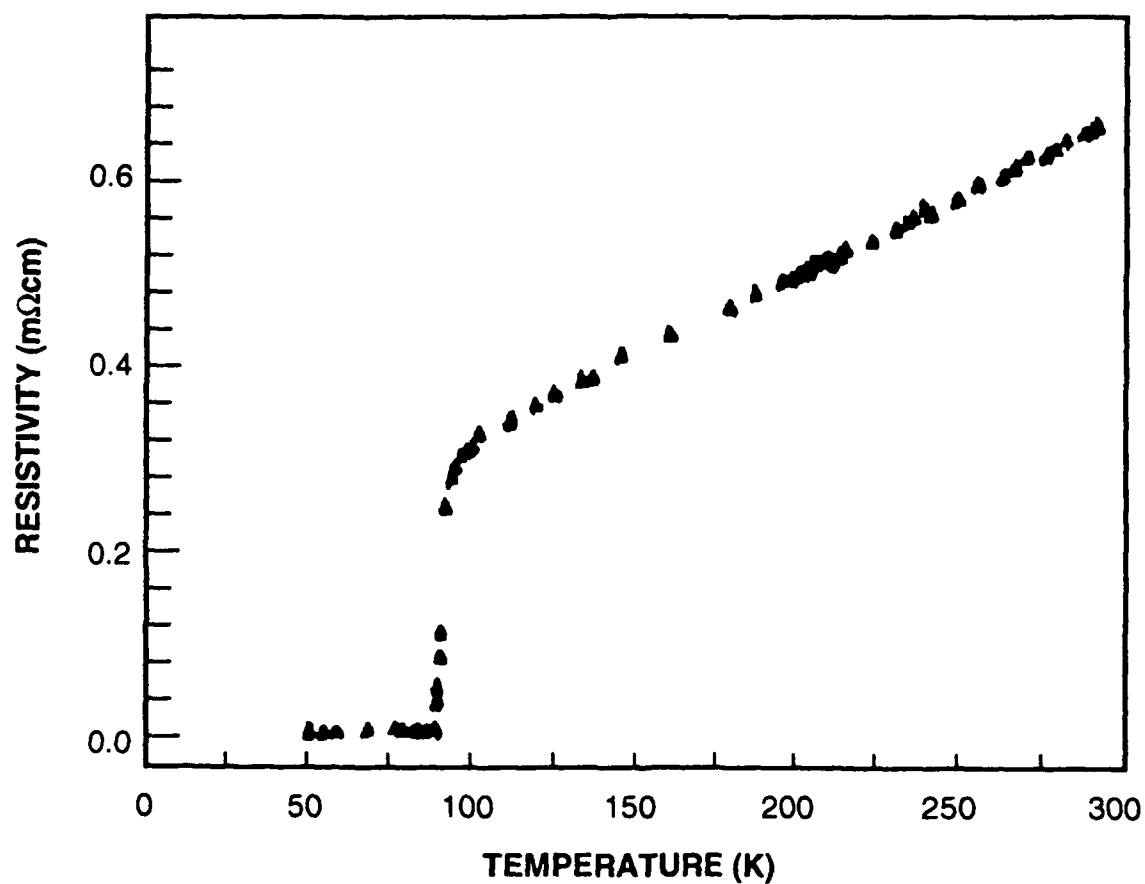
drying process gave rise to mixed precursors on an atomic scale with an average particle size of $2\mu\text{m}$. After heat treatment, undesired non-superconducting secondary phases were present at $<2\%$ and the particles formed conglomerates of crystallites measuring $20\text{-}30\mu\text{m}$. The reaction route from dehydrated nitrates to final product seems to be via the intermediate compounds Y_2O_3 and $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$. Superconducting transition temperatures with an onset at 98K were obtained with Meissner volumes as high as 44% (using a density of 3.8 g/cm^3). It is likely that with higher sintering temperatures and pellet formation pressure this could be improved significantly. A typical resistivity plot is shown in Fig. 1. A number of samples which contained large amounts of secondary phases exhibited an anomalous drop in resistivity at 240K along with a matching increase in the diamagnetic response as well as the conventional transition at 90K (Fig. 2). Reports in the literature have also indicated this with a suggestion as it being due to water absorbed into the surface of the sample. It is unclear however as to the exact mechanism involved. In conclusion, the freeze drying of nitrates provides an effective method of ensuring mixing on the atomic scale of the precursor ions resulting in high yield of very pure 123 material with extremely small and uniform particle sizes. Further details associated with this portion of the research is contained in attached reprints, preprints and the thesis entitled Synthesis and Characterizations of High Temperature Superconductors included with this report.

B) Utilization of liquid ammonia in Synthesis of ceramic superconductors.

While the principal methods used in the production of 123 powders other than conventional solid state "shake and bake" techniques rely on the solubility of the various constituent ions in water or dilute acids, these are by no means the only routes that can be taken. A useful alternative approach that was investigated in detail as part of this contract is the use of liquid ammonia as a solute. Ammonia has several advantages over conventional solvents; it has little tendency to react with its environment, control of the pH of the solution and its temperature is not critical and it gives no indication of causing phase separation of the solute materials.

Stoichiometric quantities of the Y, Ba and Cu acetates or nitrate salts were dissolved in a liquid ammonia bath at -78 C . A number of alternative procedures could then be taken. The first of these consisted of the spraying of this solution into a hot furnace resulting in the direct production of 123 material. Spraying the solution onto a surface such as a heated substrate gave a uniform thick film showing good adhesive properties and which could have useful applications in the coating of irregularly shaped superconducting microwave cavities and other large surfaces.

Spray deposits of ammonia solutions and the direct reduction and calcination of a thick film may be really used in ribbon production on an appropriate flexible



Resistivity measured as a function of time from bars cut from sintered compacts made from YBCO prepared as a powder.

FIG. 1

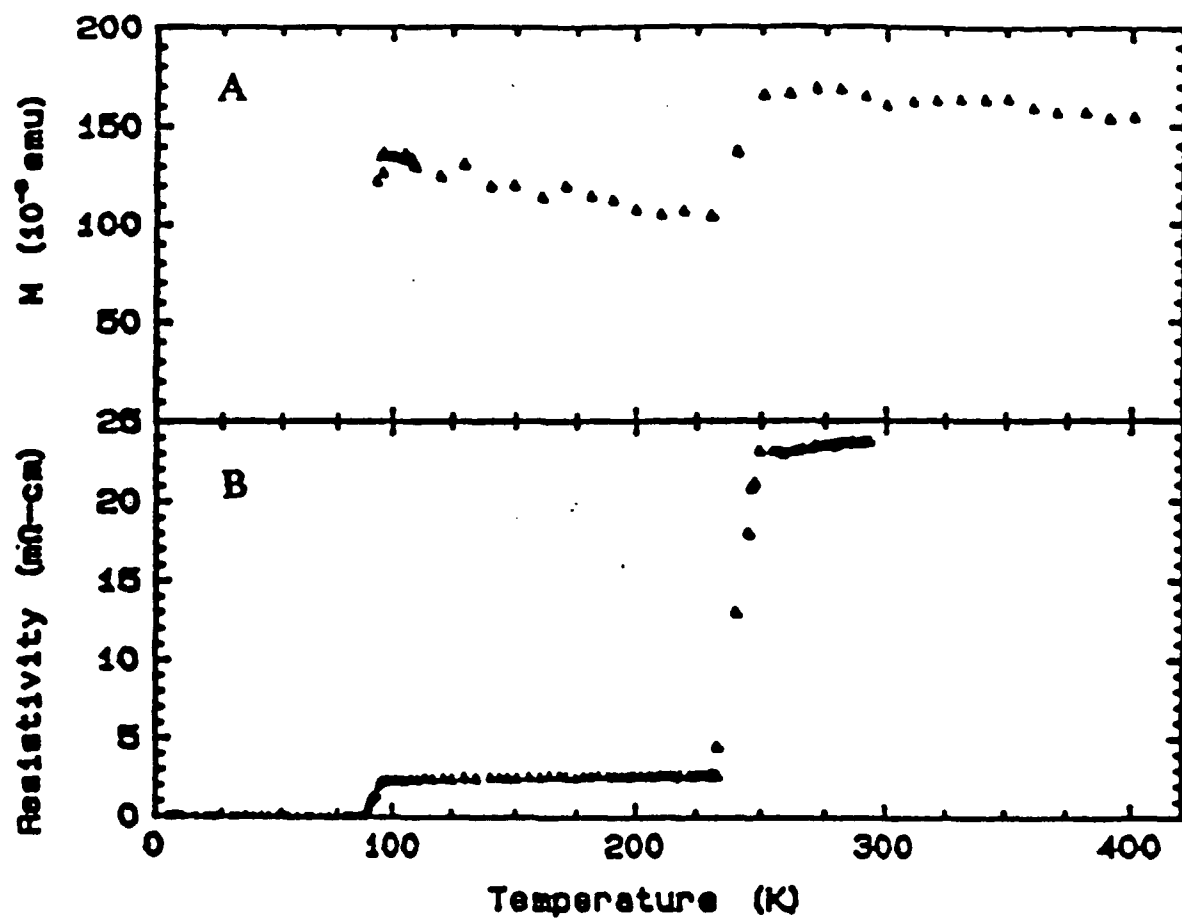


FIG. 2

substrate such as the recently produced flexible ZrO_2 ribbon produced by General Electric, Inc.

An alternative method of obtaining 123 from the ammonia solution is by reaction with CO_2 , either in solid or gaseous form, to form a carbamate. In the former, the ammonia solution is sprayed onto a bed of dry ice. The resultant material can be left to warm to room temperature with the consequent sublimation of everything but the precursor material. Alternatively, gaseous CO_2 can be bubbled through the ammonia solution giving a white precipitate. This powder can be filtered off and fired to produce high purity 123 material. Phase separation during this processing appears not to be a problem whereas it does present difficulties with many of the other solution based techniques. In addition, the precursors have unusual properties which may prove to be useful in applications adaptable to unreacted precursors.

C) Sol-Gel Synthesis of ceramic superconductors.

Preparation of ceramic superconductors using the much publicised "shake and bake" method can be expanded to produce large quantities of high purity powder. It is however, labour intensive and time consuming and does not lend itself to the mass production of powder in quantities such as that required if ceramic superconductors are to be used in everyday technological applications. The quality of the product resulting from such a method is measured in part by the particle size that results from the continued grinding and regrinding process, however, particular care must be taken to avoid mixing of the constituents with contaminants from the grinding process. Methods that result in a similar quality powder without this time consuming process are likely to result in a cheaper and more widespread use of ceramics, and may prove to be more adaptable to commercial areas.

Such a method is found in the use of sol-gel techniques. A typical processing schedule consists of mixing stoichiometric solutions of the acetate salts of Y, Ba and Cu in water and then adding 2% by weight of a gelling agent to the warm solution to 'set' the mixture. A number of protein or sugar agents were experimented with including Agar, pectin, carboxymethylcellulose, gelatin, alginic acid, xanthan gum, guar gum, carrageenan and tamarind gum. Of these the most successful results were obtained from gelatin. After gelling, the sample is dehydrated to form a Xerogel precursor which is then thermally processed by heating to 900 C for 24 hours. All of the organic gel material burns off during firing. As the gels form, the metallic ions of the nitrates are trapped within a network of the gel material. When this is ground in a conventional ball mill and the gel removed during the heating process, the ions are left as an even finer form than the gel-ion particle size ($<1 \mu\text{m}$ determined by SEM). After initial sintering at high temperatures, superconducting yields were ~70% with zero electrical resistance occurring at 70K. After final processing in flowing oxygen at 500 C, superconducting yields were ~ 100% with T_c at 90K. This

method of powder production is extremely useful in the studies of impurity interaction as very small concentrations of dopants can be added to the initial solution with a very isotropic powder resulting. Also, the dried and powdered gel-solution appears to be quite stable under long term handling with only minor precautions taken to protect the precursor. The stability of this precursor may be useful to certain applications.

D) The Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ from fused hydroxides.

As in the case of the preparation of 123 precursor mixtures utilizing freeze drying as discussed above, the method of synthesis of the 123 material from fused hydroxides focuses on the elimination of the mechanical mixing, multiple grinding-calcining cycles with their consequent introduction of carbon containing reagents which is common in most other methods.

Preparation consisted of heating stoichiometric quantities of Y, Ba and Cu nitrates to 230 C under nitrogen with solidified eutectic of potassium and sodium hydroxides. At ~190 C, the reactant containing eutectic melted forming a black solution. After 72 hours the reaction medium was cooled and dissolved in cold water. The resulting black precipitate or precursor was washed and dried in air. Batches of the powder were calcined in a box furnace for 24 hours at various reaction temperatures. Average particle size of the precursor is ~1 μm . Temperatures of 900 C are required to produce single phase (<2% impurity) 123 with a consequent oxidization at 500 C for 6 hours to ensure superconductivity. Typical transition temperatures of 123 formed with this method are ~90K with superconducting fraction of 47% as measured by magnetization in a 100G applied field. Tests to ascertain the sensitivity of this method to water content of the eutectic showed that even small water contents caused a substantial loss of barium in the product. The apparent superconducting fraction depends critically on the applied magnetic field and substantially increases as the field is reduced. A fixed measuring field of ~100G has been used in most of these studies as a comparative measure of sample quality.

This method produces fine 123 precursor material consisting of $\text{Y}(\text{OH})_3$, BaO_2 and CuO from a solution of nitrates which, without the oxidizing eutectic would require temperatures in excess of 600 C to promote breakdown of the nitrates. By eliminating the high temperature stage and the grinding and mixing stages there are real possibilities for a much improved economically viable method of mass production of superconducting 123. It is however very sensitive to the water content of the eutectic.

While the above method demonstrates the utility of fused hydroxides, it necessarily involves the use of water to remove the precursor from the solid eutectic mixture. This aspect of the process ultimately interferes with the synthesis of the product. The use of barium hydroxide is much superior as this material used as both flux and reactant is consumed in the reaction. Although barium hydroxide has been utilized in the preparation of 123 before, it was present only as an

alternative source of barium in the reaction. In this case, the low melting (78 C) octahydrate hydration state is used as a solvent for the nitrates of Y and Cu, while the anhydrous form (mp = 408 C) serves as a medium for mixing and as a reactant with complete decomposition occurring during the subsequent thermal processing.

A typical reaction route consisted of melting stoichiometric quantities of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, anhydrous $\text{Ba}(\text{OH})_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ in air. Once a completely liquid mixture was obtained, this was heated more strongly until complete reaction had taken place as indicated by a black solid precursor. This material was lightly crushed and formed into a pellet and sintered in air for 18 hours at 950 C. Oxygenation took 5 Hours at 500 C. Samples of this material exhibited zero resistance at 91 K with T_c onsets at 95K. Xray analysis indicated impurity phases to be <1% of the total volume. It is noted that a limitation of this technique is that the sample must be heated uniformly especially at the stage where the precursor begins to solidify from the high temperature melt. Inhomogenous heating results in concentration gradients appearing in the powder with a consequent degradation in the superconducting properties. This may ultimately prevent this method from becoming a viable commercial mass production enterprise it remains a useful reaction route for obtaining high purity samples on the laboratory scale.

The fused hydroxide solvent system is not limited to the production of 123 but has general utility in other metal oxide superconductors. The high boiling points of the fused hydroxides and salts permits access to high temperature solution chemistry. Compounds whose formation might otherwise be inaccessible in aqueous solutions at low temperatures might well find the necessary conditions in the fused hydroxides.

III) Thick Film Fabrication and Characterization

The examination into the properties of thick film superconductors has taken a substantial portion of the resources of this project. The various aspects of this work can conveniently be broken up into a number of topics listed below.

- 1) The effect of conventional thermal treatment and melt texturing on the superconducting properties of thick films with particular attention given to critical current, $J_c(T)$ and zero resistance temperature, T_c and their dependence on microstructure. Also, a portion of this section of the program was devoted to studies of the introduction of liquid phase sintering agents on the superconducting properties of bulk processed thick films.
- 2) The effect on superconducting properties of substrate interaction and impurities. Some of the impurities studies were focused on classifying the effects that various Cu-site and non Cu-site impurities have on

both normal and superconducting properties. Such study is critical to the evaluation of impurities on enhancing superconducting properties such as pinning and flux stability.

- 3) The interaction between thick films and electrical contact materials and the effect on superconducting properties. Normal-to-superconducting terminations are critical to hybrid microelectronics applications.
- 4) The uses of protective coatings to prevent environmental degradation of the superconducting properties after fabrication and device development.
- 5) Surface Impedance measurements to explore the utility of thick film processing for large scale microwave applications.

Where possible all characterization tests on materials including resistance as a function of temperature, critical current, infrared response, contact material suitability, microwave absorption, X-ray and electron microscopy were performed on the same thick film sample. To assist in this, a single 2 inch by 1 inch substrate printed with a specially designed test pattern was used for testing (see Fig. 3) giving a variety of different thick film configurations. Several other test patterns were fabricated to provide a variety of test configurations.

A second subsidiary section of the project involved the design and fabrication of actual high temperature superconducting devices.

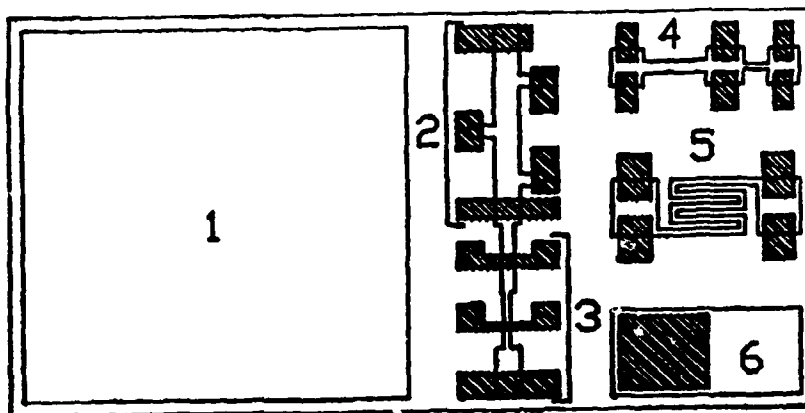
A) Preparation and Fabrication based Research.

- 1) Conventional thermal treatments, rapid thermal processing and melt texturing of thick films.

Numerous substrate materials, including 96% Al_2O_3 , pure Al_2O_3 , MgO , SrTiO_3 and ZrO_2 were investigated for possible application in superconducting thick film processing. In addition, a variety of buffer or barrier layer systems, including Ag , LaAlO_3 , BaZrO_3 , CaF_2 , YF_2 , and BaF_2 , were studied. Results of substrate reaction studies are included in the next section. The most promising substrate material was found to be Y stabilized ZrO_2 . Thick film processing results using the other substrate systems are contained in previous reports and are not summarized here.

A number of the properties of thick film samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) produced on Yttria stabilized Zirconia (YSZ) substrates were studied as a function of sintering temperature T_s for $930 \leq T_s \leq 1010$ C. All the films were produced from a frequently used shake and bake powder using conventional screen printing and belt furnace drying techniques, the only variable being the temperature of final sintering.

THICK FILM SUPERCONDUCTOR PATTERN



1. X-ray Diffraction Specimen.
2. Four Point Resistivity Measurement Specimen.
3. Contact Resistance Measurement Area.
4. Critical Current Density Specimen.
5. IR Response Measurement Specimen.
6. Microstructural Analysis Sample.

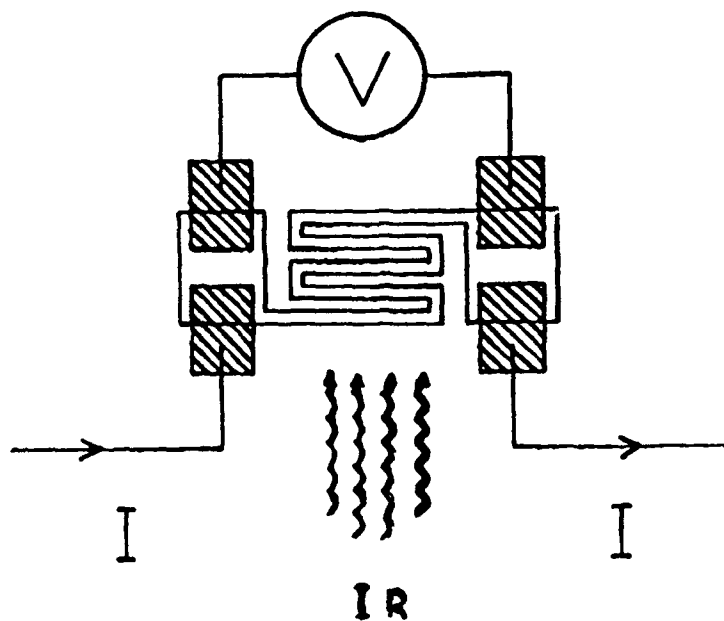


FIG. 3

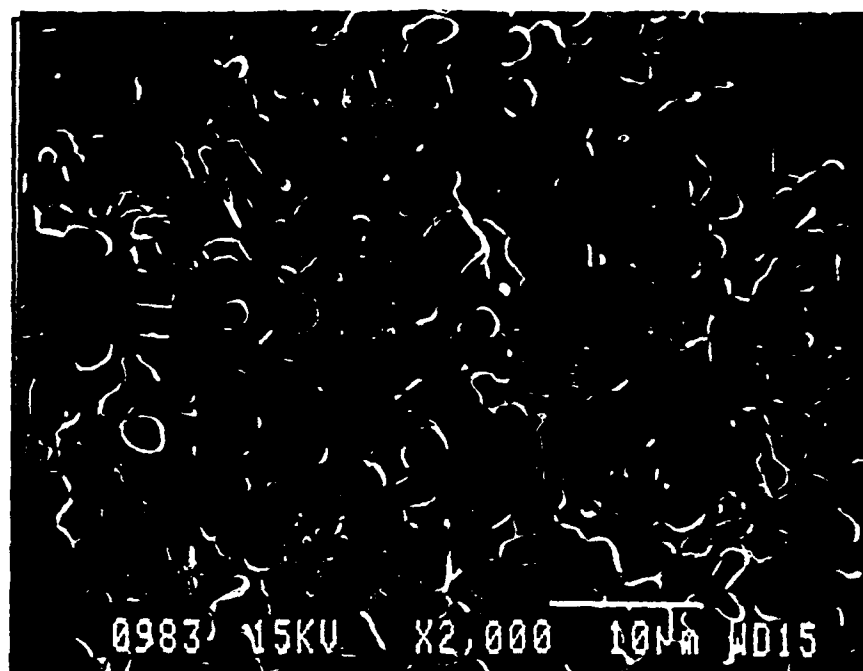
Xray patterns indicate that sintering temperature has only a small effect on the amount of preferred orientation of the grains on YSZ. This result is not consistent with results from similar studies on other substrates where substantial preferred alignment with the C-axis perpendicular to the film plane was observed, e.g. Al_2O_3 (see previous reports). Electron micrographs show a distinct change in morphology of the film as T_s is increased. The film can be seen to change from a fine powder conglomeration to a collection of larger more irregularly shaped and orientated crystals (Fig. 4 a and b). Sintering temperatures much below 930 C revealed a high percentages of unwanted second phases or gave inadequate adhesion between the film and substrate.

Resistivity measurements indicate that the transition temperature changes vary little but the width of the low temperature resistivity tail decreases with increasing T_s (see fig. 5). Below $T_s=980$ C, the critical current at 77 K does not exceed 10 A/cm^2 , however J_c increases sharply with sintering temperatures above 980 C reaching 1000 A/cm^2 for $T_s=1010$ C (Fig. 6). Higher J_c values close to 2000 A/cm^2 have been achieved in limited cases with T_s in the vicinity of 1010C.

Further Xray measurements indicate that the sintering temperatures promote the formation of secondary phases and we would infer from this and the J_c data that the presence of these secondary phases aids in the sintering of the grains with a consequent decrease in intergrain scattering.

Techniques of rapid thermal processing of superconducting thick films were investigated as a means of limiting diffusion of impurities into the superconducting materials both from the contacts and the substrate. These methods relied on the rapid melting and quenching of lightly sintered film samples, radiative heating at the facilities of Process Products Inc. in Boston, MA. In the latter case, samples presintered to alumina substrates at 580 C, were heated to temperatures ranging from 950 C to 1200 C for 10 to 30 seconds at peak temperature. All of the films showed extensive cracking due to thermal shock and loss of pattern definition due to melting. Films presintered to 930 C retained greater definition. Samples on MgO substrates had a tendency towards shattering due to thermal shock. Resistivity and J_c measurements indicated results consistently worse than conventionally process films, or melt texturized samples.

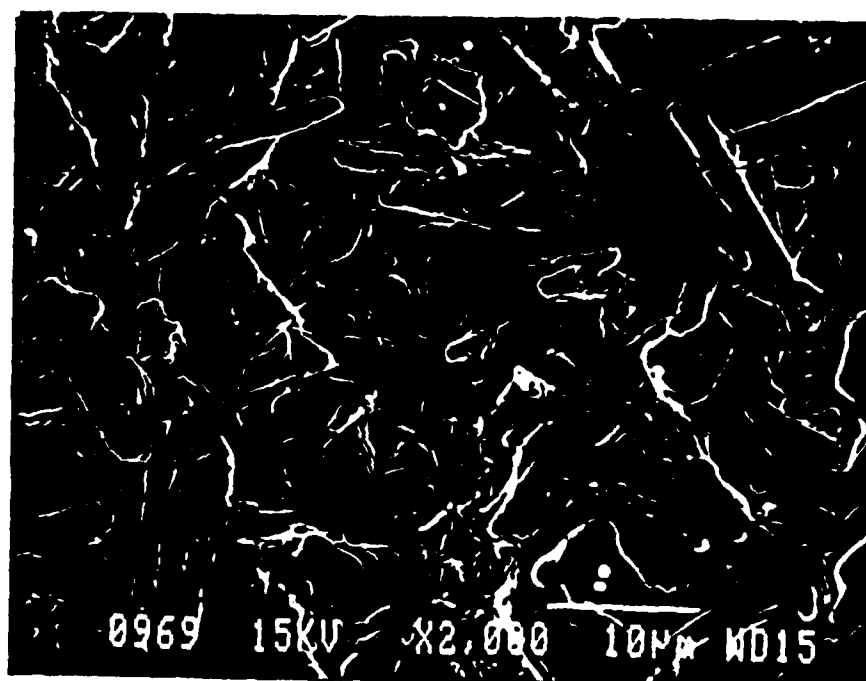
Investigations into the possible utilization of liquid sintering techniques to densify the superconducting ceramics and thus increase the current carrying capacity were assisted by Dr. Joseph P. Teter at the Naval Surface Warfare Center at Silver Spring MD. Bulk samples of $(\text{Y}_{1-x}\text{Dy}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$ ($0 \leq x \leq 1$) were prepared from $40\mu\text{m}$ powders with an added 5% $\text{Ba}_2\text{Cu}_7\text{O}_7$ (2-7) low melting phase (mp 880 C). The materials were fired at 925 C and 950 C for 5 hours. Control samples without 2-7 were heated to 950 C for 5 hours. In all cases the porosity of the fired samples was



$T_F = 950\text{ c}$

$\text{YBa}_2\text{Cu}_3\text{O}_7$

Substrate: Ys Zr O_2



$T_F = 1025\text{ c}$

$\text{YBa}_2\text{Cu}_3\text{O}_7$

Substrate: Ys Zr O_2

FIG. 4

THICK FILMS ON Y STABILIZED ZrO_2

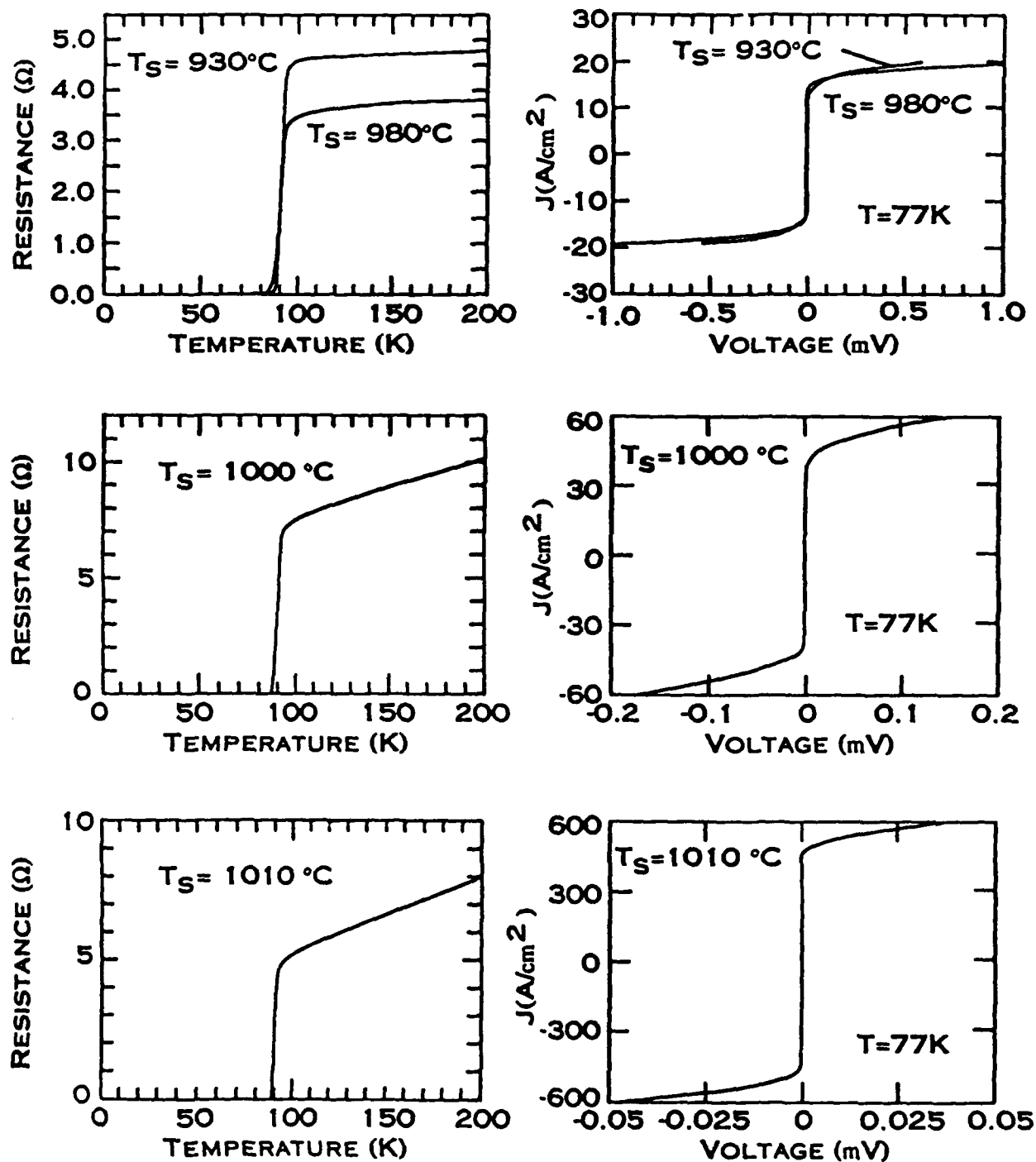
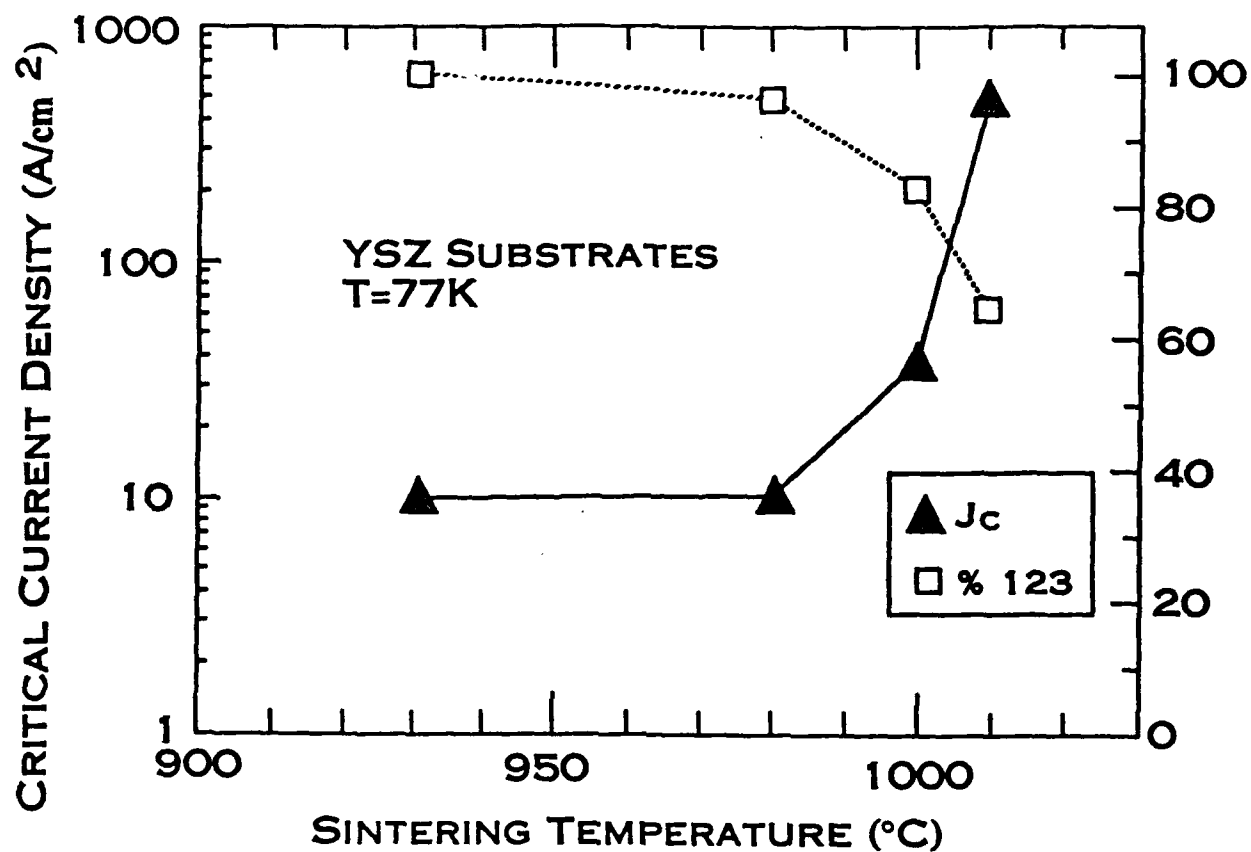


FIG. 5



$T_C / \text{ZERO} \approx 89\text{K}$

FIG. 6

less than the prefired state, although samples with $x=0$ and $x=1$ showed less densification than intermediate values of x . The addition of 2-7 had little effect on sample density for samples fired at 925 C. Firing to 950 C with the 2-7 addition did show enhanced densification.

After post annealing in flowing oxygen at 600 C for 18 hours, critical current in all the samples was measured using a vibrating sample magnetometer technique. For samples fired at 925 C the addition of 2-7 had no observable effect on the magnitude of J_c . In contrast, the samples fired at 950 C all showed significantly higher critical current. The addition of 2-7 had little effect on J_c for the Y rich materials ($x<0.5$) but increased the fully substituted Dy material from 4252 A/cm² to 11786 A/cm². The highest J_c 's were obtained from the $x=0.5$ concentrations fired at 950 C with and without addition of 2-7 giving values of 15346 A/cm² and 18520 A/cm², respectively.

The enhancement of J_c can be attributed to the formation of solid solutions in the Y-Dy 123 system which create point defects or flux trapping centers as a result of crystal lattice distortion. This distortion is caused by the mutual substitution of Y and Dy with their two differing ionic radii (0.097 and 0.088 nm respectively).

A further study into liquid phase sintering of the thick film samples was undertaken using the non-superconducting phase YBa₄Cu₁₀O_x (1410) produced at Temple University. This was blended at 4% and 10% by weight with a commercial powder from CPS. A series of films were printed on alumina substrates and fired at 850, 930 and 980 C together with pure CPS powders as controls. After oxygenation, resistivities and critical currents were measured with a conventional four probe technique. At the 4% level, the addition of 1410 enhanced the critical current of the material by a approximately a factor of 2-5. At the 10% level the performance was degraded below the level of the pure material. In both cases T_c was lowered by the addition of 1410.

Addition of silver oxide 99.99% (Ag₂O₃) at the 2% and 5% level to a commercial 123 powder in this case W.R. Grace, met with more encouraging success. This impurity has often been cited in the literature as increasing grain growth and enhancing critical current. Increases in J_c of up to a factor of 50 were obtained for the 5% doped samples on alumina without the depression in transition temperature observed for the 1410 phase. The J_c value though improved remained less than the values obtained from conventionally prepared 123 thick films on ZrO₂. Degradation of superconducting properties was observed however for similarly prepared films on SrTiO₃ and MgO.

Reports from Los Alamos National Laboratory indicate that the impurity content of 123 can be reduced by a thermal cycling of the samples between 940 C and 890 C. A study of this technique was undertaken. A typical processing included

taking the pressed pellets of mixed oxides and cycling over the temperature range every four hours for 7 days. The pellets would be reground, repressed and cycled for a further 2 days. After reforming again the samples would be placed in a furnace at 430 C, taken to 960 C over 6 hours, left for 24 hours, cooled to 430 C, cycled back to 960 for 6 hours and then cooled to 430 C for oxygenation over 7 days. No evidence for substantial improvement in the superconducting properties of thick films was observed.

2) The effect on superconducting properties of impurities and substrate interaction.

A complementary program which paralleled the device focus of the main thrust of this project was studies of impurity effects within the broad class of high T_c superconducting oxides. These studies were driven by the need for a clearer understanding of the impact that certain impurities could have on the superconducting properties and the need for compatible barrier and substrate systems. The benefits associated with these studies include a better understanding of site sensitive impurity effects on both the superconducting and normal state properties and the development of systems that may prove critical in the engineering of weakly coupled devices and a barrier systems, e.g., $\text{PrBa}_2\text{Cu}_3\text{O}_7$, $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$, $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_8$ with $\text{M}=\text{Y}$, Pr and Gd , etc. Recall, impurities studies have played and continue to play a crucial role in the development of commercially viable low T_c systems, e.g., impurities and impurity clusters are essential to enhanced pinning in both Nb-based alloy systems and in the A15 structures. Even with the discovery of the new high T_c oxides, work within many Japanese and Europe laboratories is continuing on impurity driven enhancement of the high magnetic field current carrying capacity of both A15 and Cherlev phases.

Shortly after the discovery of the high T_c oxide superconductors, it was abundantly clear that these new structures and their superconducting properties were very sensitive to minute impurities and that to obtain the most favorable thick film properties and device performance required high temperature processing. Such high temperature processing made contamination through substrate interaction a critical issue. In addition to the substrate interaction issues, it was critical to understand the site sensitive nature of these new structures to identify possible routes to enhanced pinning and possible morphologically similar structures for substrate and barrier layer applications. These impurity studies were supported primarily by leveraged support provided by the Ben Franklin Partnership Program of the Commonwealth of Pennsylvania and the Center of Materials Research and Technology at Florida State University.

The impurity studies focused on three primary areas which included (1) site sensitive impurities studies with primarily attention given to Cu-site dilution by other transition metal ions, e.g., $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-y}$ with $\text{M}=\text{Ga}$, Al , Cr , Ni and Zn ,

(2) control modification of superconducting properties within $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other high T_c systems without disrupting structure, e.g., $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_8$ with $M = \text{Y, Pr and Gd}$, and (3) study of substrate interactions and compound formation at superconducting-substrate interfaces. The studies of Cu-site sensitive dilution clearly indicated that most impurities that enter the Y123 structure on Cu-chain sites lead to only small changes in superconducting properties and structure whereas impurities doped onto Cu-plane sites lead to a drastic depression of the T_c due to a breaking of the highly correlated Cu-O hybridization which leads to a localization of the carriers. It identified Zn-doped Y(123) as a likely candidate for barrier layer application. For Zn concentrations exceeding 10%, superconductivity is depressed and carriers are localized with the resistivity changing by 3 orders of magnitude in the vicinity of 10% Zn. The resistivity changes are more dramatic than observed in Pr-doped 123. An unexpected outcome of this research was demonstration that these systems have considerable potential as catalytic systems for several important chemical processes, e.g., the catalytic ammoxidation of toluene and the kinetics of CO oxidation. The second phase of our program that focused on the identification of morphologically similar systems for use in barrier layer engineering and as a possible substrate system have been extremely

A chemical analysis of the exact composition of the substrates normally used for fabrication of high temperature superconducting thick films was considered to be of primary importance. Many commercially available materials contain impurities that are recognized as being responsible for the degradation of superconducting properties. Among those materials investigated were alumina of various purities, Yttria stabilized Zirconia (YSZ), MgO , SrTiO_3 , CaF_2 , YF_2 , BaF_2 , ZrO_2 , GaAlO_3 and LaAlO_3 together with numerous barrier layer systems such as CaF_2 , YF_2 , BaF_2 , Ag and Au. These materials were obtained from a variety of sources. In the choice of polycrystalline substrate systems, it was felt critical to have the substrates commercially available or, at least, readily developable by commercial suppliers. We have worked closely with several manufacturers and suppliers in the development of possible substrate materials. An effective and reliable test procedure was needed to evaluate possible substrate superconductor reactions. A typical test procedure consisted of blending $\text{YBa}_2\text{Cu}_3\text{O}_7$ with 20% by weight powdered substrate material and heating to 700, 800, 900, 950 and 980 C. The samples were then evaluated to determine the resulting phase composition.

When heated to temperatures of 900 C and above, the alumina, La and Ga aluminate substrates encouraged the formation of a substantial portion of the insulator BaAl_2O_4 , SiO_2 present as an impurity in alumina gave traces of BaSiO_4 . MgO showed 4-5% of Y_2BaCuO_5 at 900 C, while calcium and yttrium fluorides reacted with the superconductor to form BaF_2 and a variety of other non-superconducting phases leaving no trace of the original 123. The presence of Zr in the substrate material encouraged the formation of BaZrO_3 . SrTiO_3 reacted strongly with the material producing a variety of non-superconducting phases.

In a similar study, the effect of substrate material on the electrical transport properties of 123 was also performed. Regular screen printing process uses conventional shake and bake prepared powder was used in the fabrication of thick films patterns on a number of different polycrystalline substrates; 96% and 99% purity Al_2O_3 , 95% MgO , YSZ and SrTiO_3 . Xray and electron micrographs of films reveal that changes in sintering temperature have little effect on preferred orientation of the crystallites in all but the case of Al_2O_3 which sees a dramatic increase for temperatures greater than 940 C (Fig. 7). Despite this high degree of alignment, T_c for alumina based films remains low in the range of 50-70K and J_c does not exceed 200A/cm² at 4.2K. Samples sintered below 950 C show semiconducting like resistance above T_c . Thick films prepared on MgO and YSZ have sharp resistive transitions with $T_c \approx 90$ K and metallic resistive behavior above this. The critical current densities are much improved over alumina but remain low in comparison to thin film measurements. The best results have been obtained for MgO where $J_c \approx 2000\text{-}2500$ A/cm² at 4.2K measured with a conventional 4 wire resistance experiment to a resolution of 10^{-8} V. Films produced on SrTiO_3 gave low and broad transition temperatures similar to that observed for alumina. This has been reported in the literature as being due to the diffusion of Sr into the superconductor

To reduce or eliminate the generally detrimental effects of substrate interaction, a variety of diffusion barriers or buffer layers were investigated. Thick films of barium aluminate and barium peroxide were fired onto alumina substrates at 980 C. Conventional preterminated superconducting 123 films were then layed down and fired at 930 and 980 C. The samples with barium aluminate buffer layers underwent considerable melting even at 930 C, giving rise to extensive patches of the non-superconducting so called "green" phase Y_2BaCuO_5 (211). Films fired on BaO_2 also exhibited considerable melting with production of secondary and insulating phases. Superconducting films were also layed down on MgO and stainless steel substartes utilising diffusion barriers of silver together with silver contact material. After firing, these too showed substantial quantities of the 211 phase even for low reaction temperatures.

3) The interaction between thick films and electrical contact materials and the effect on superconducting properties.

A series of samples was produced on MgO substrates with three different commercial thick film conductor compositions. (ESL #8880 Au, #8884 Au and #9990 Ag). Contact resistances were measured using a quasi-four probe technique allowing the resistance of any single contact to be evaluated. To determine geometric effects, three different contact geometries were produced and processed simultaneously with no observable difference in specific contact resistance R_c being noted. Tests on

PERFERRED ORIENTATION OF THICK FILM ON VARIOUS SUBSTATES

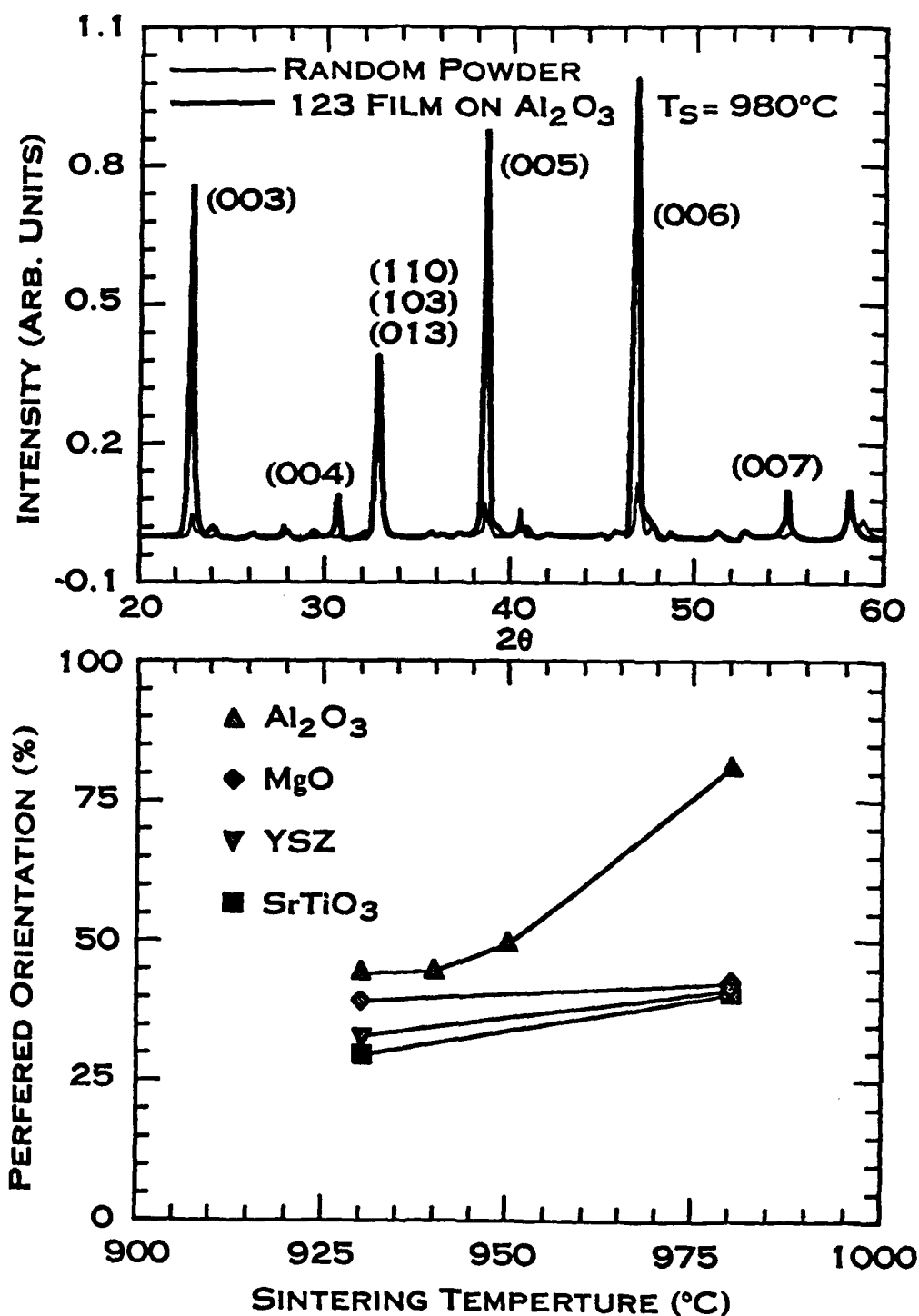


FIG. 7

both pre-terminated (application of the contact to the substrate before the superconducting film) and post-terminated (application after the film) have been observed. The principal difference in the two methodologies is that in the case of the pre-terminated contacts, the contact forms a layer between the substrate and the superconducting material. For the post-terminated case, the contact is printed over the superconducting film.

In Fig. 8 a the specific resistance of all three conductors is plotted as a function of temperature for superconducting films fired at 930 C. The substrates were all preterminated, the gold being fired at 980 C and the silver at 850 C. R_c of the Ag contact drops rapidly as the film becomes superconducting and levels out at a value of $1.4 \times 10^{-10} \Omega \text{ cm}^2$ at 50K ($3.5 \times 10^{-8} \Omega \text{ cm}^2$ at 77K). For reasons not understood, the resistance of the gold contacts fluctuates when the film is in the superconducting state with a mean value of $\sim 10^{-8} \Omega \text{ cm}^2$ at 77K. For films sintered at 980 C (Fig. 8 b), the contacts show the similar anomalous fluctuating behavior with a mean value $\sim 10^{-7} \Omega \text{ cm}^2$.

A comparison of the differences between pre and post-firing terminations (Fig. 8 c) for Ag contact films indicates that the post terminated films have an R_c a factor of ten greater than the pre-terminated specimen. Fig. 8 d shows the difference in contact resistance obtained when post-terminated films are fired at 930 and 980 C. Higher temperatures result higher resistivities when the film is in the normal state. This may well be due to the higher amount of diffusion of the silver into the superconductor due to the higher sintering temperature.

4) Environmental Stability and Protective Coatings.

The problem of the environmental stability of high temperature superconductors is well known. The superconducting properties of the 123 compound in particular, are found to degrade substantially within days if left exposed to ambient atmosphere. In sintered thick films where extensive milling of the precursor powders results in more complete solid state reaction and superconductor yield, this same preparation gives rise to a high surface area to volume ratio and thus preponderance to environmental degradation of the sintered material.

Comparisons of firing schedules performed in humidified air and dry air revealed substantial negative effects on the electrical properties both in the normal and superconducting state. Storage of samples in a controlled high humidity chamber also showed much inferior electrical characteristics than those in dry boxes. Electron microscopy and Xray analysis reveals that water reacts with the film to produce barium hydroxide, an insulator that disrupts the electrical current paths between grains.

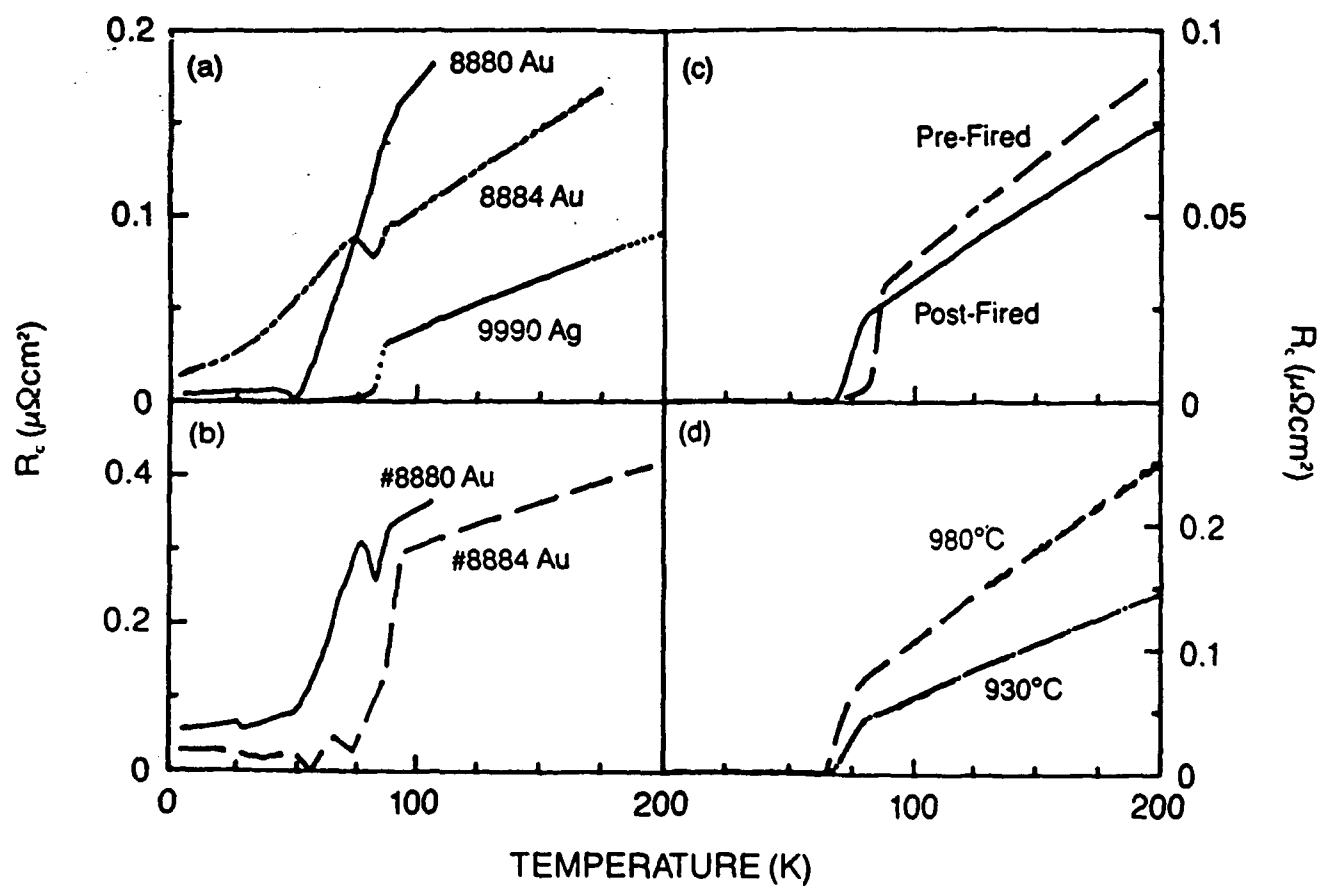


FIG. 8

A number of polymeric coatings were investigated. These materials are designed to be screen printed across the superconducting film after its high temperature sintering, thus forming an air tight seal across the sample and also giving a high degree of protection from physical damage. Results indicated that after initial degradation of electrical properties immediately after application, excellent stability was achieved for the propriety ESL 240-SB and ESL 242-SB polymers. After storage at 85 C in 85% humidity no degradation was observed, this contrasting strongly with unprotected samples.

B) Device Development

1) Infrared Detectors

The possibility of using a HTSC thick film of YBCO was investigated for possible IR applications. There are two types of IR responses expected for this material; an intrinsic and a bolometric response. Figures 9, 10, 11 and 12 show respectively the operating principle of the sensor, the experimental set-up used for the measurements, a model for the bolometric response and a model for the intrinsic response. The operating principle of a bolometer is the resistance change produced in the sensor when it is illuminated with IR (heat) radiation. The operating principle for an intrinsic IR sensor is the change in the IV characteristic of a single junction(1) in the presence of IR radiation. This change results from the dependence of the order parameter of the superconductor on the number of quasiparticles in the system, which in turn depends on the amount of IR radiation impinging the superconductor. The multi-granularity of our films, could then offer the potential for a large intrinsic response. A small intrinsic response was observed in our film together with a larger bolometric response as is described below.

A meander pattern was made with 123 paste fired at 980C onto a 5 mill thick single crystal sapphire substrate. This type of pattern would have the effect of maximizing the number of junctions exposed to a given amount of IR radiation. The superconducting film was made as thin as possible (30 microns), to minimize the number of junctions not exposed to IR radiation.

The experimental arrangement is shown in figure 9. A black body was used as the source of IR radiation, mechanically chopped so as to enable the frequency dependence of the sample to be measured and lockin detection to be utilized. The sample was cooled by mounting to the cold stage of a closed cycle refrigerator.

The resistive transition of the film used in this study is shown in figure 10. Figure 11 shows the temperature dependence of the normalized temperature derivative of the resistivity curve together with the current derivative of the voltage signal. For a pure bolometric signal, both curves should track each other. From the data one can observe three distinctive features. 1) Both curves track each other closely through out their entire span. 2) There is a clear shoulder in the low

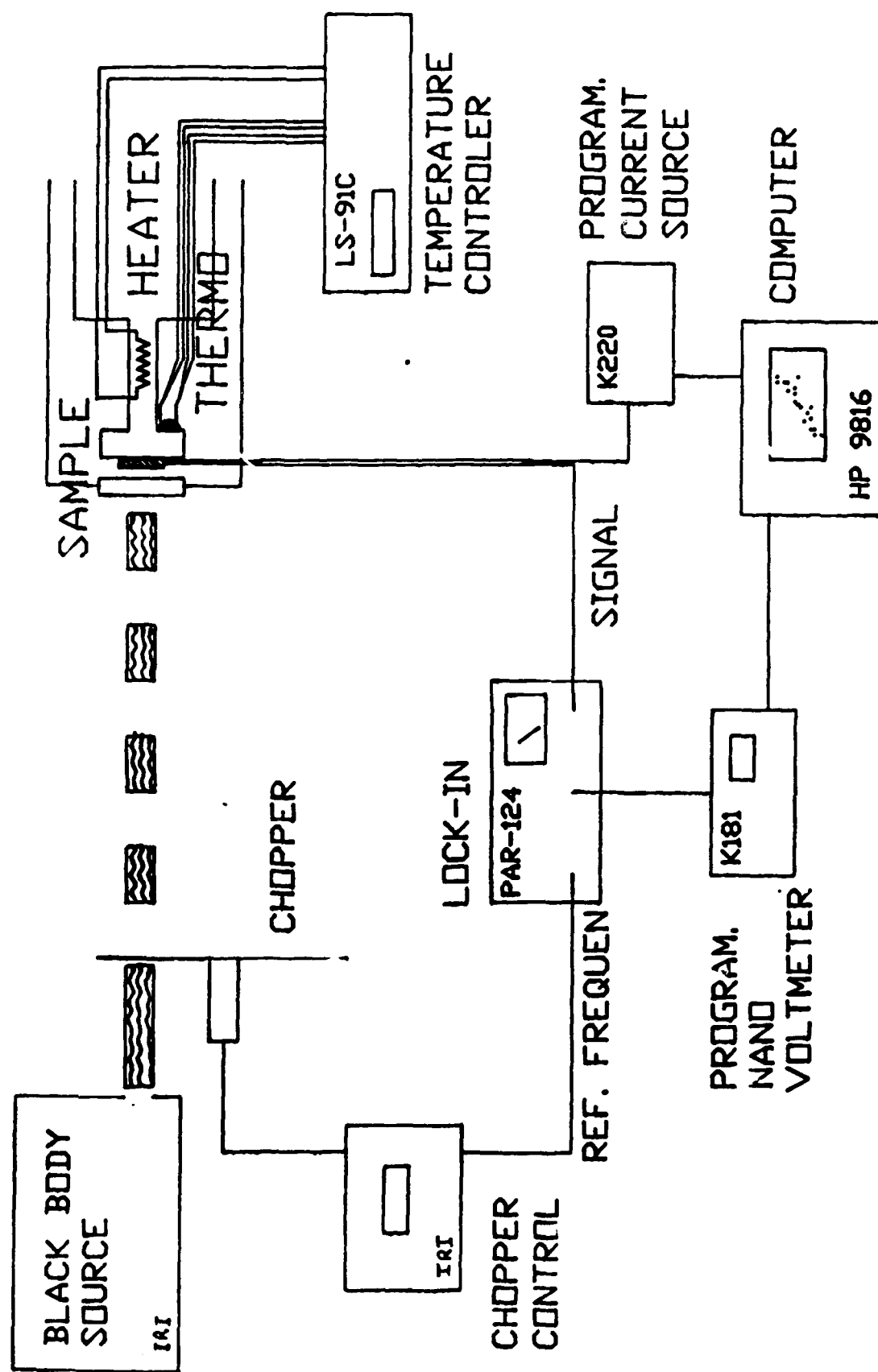
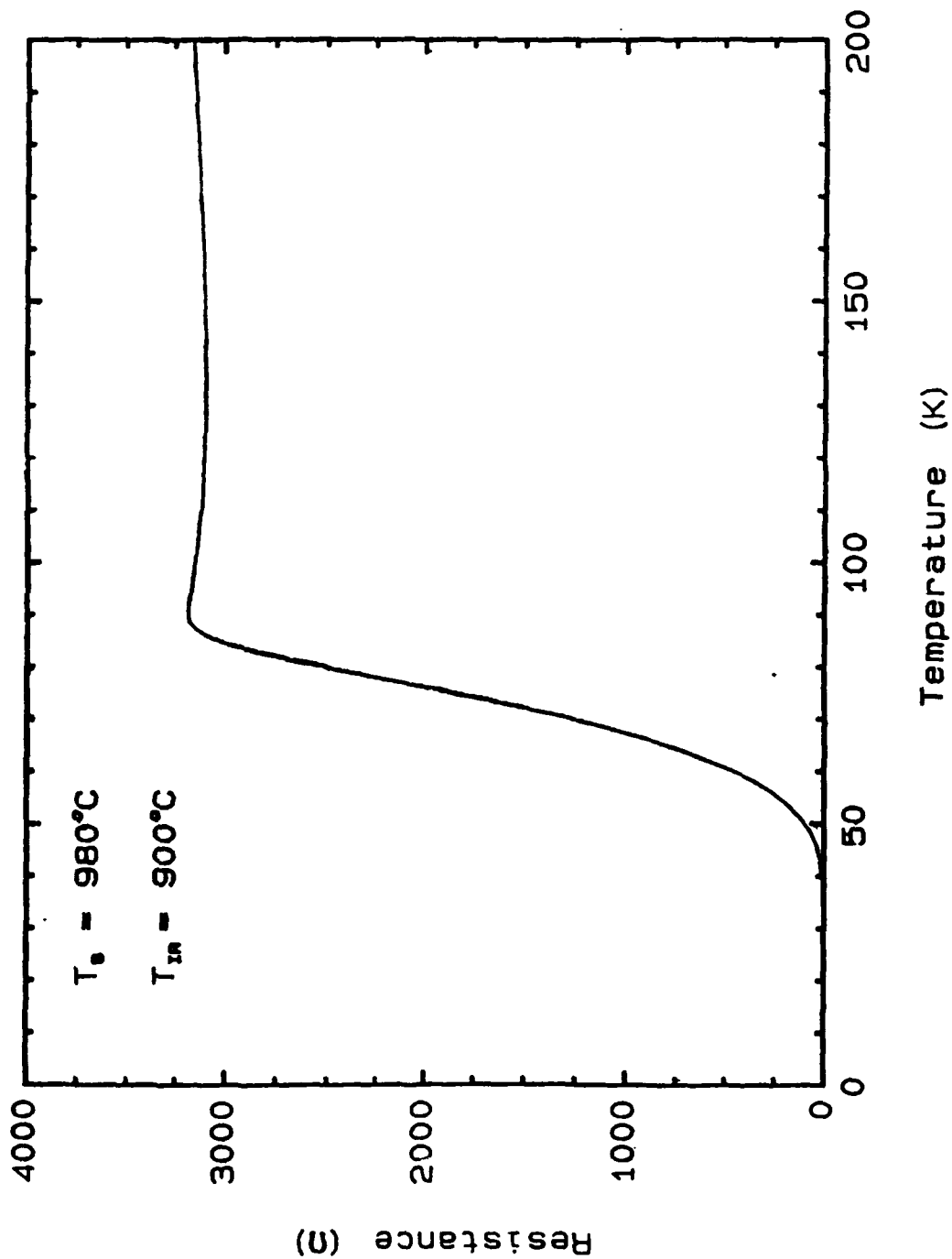


FIG. 9

89_194 (30 μ m thick 1.2.3 film on 5 mil Sapphire Substrate)



- THIN SUBSTRATE
- $T_c \approx 77K$

FIG. 10

$$V_3 \propto I \frac{dR}{dT}$$

• BOLOMETRIC

• HUM P $\approx T = 50K$

$$R = \frac{V}{P} = 1.1 \frac{V}{W}$$

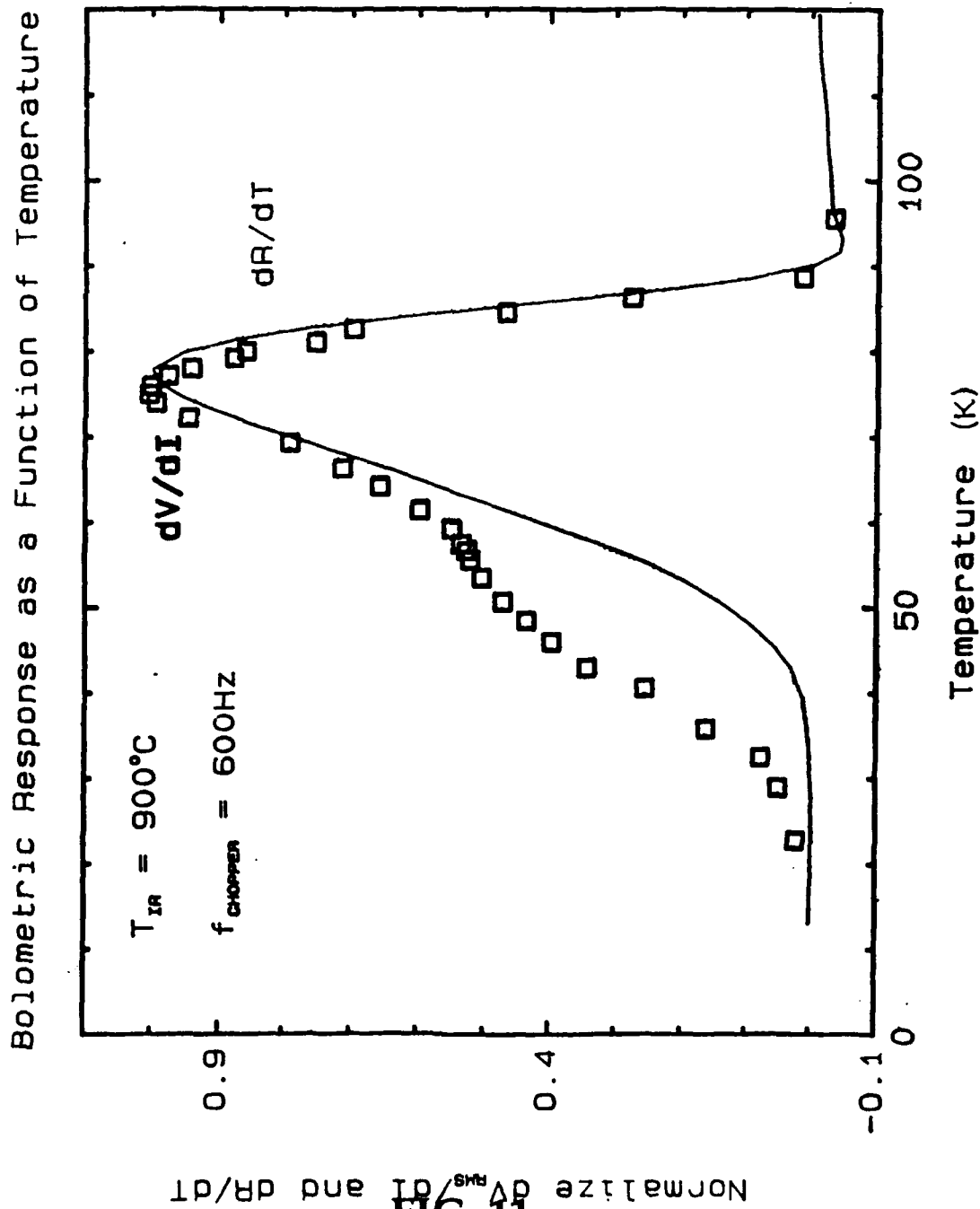
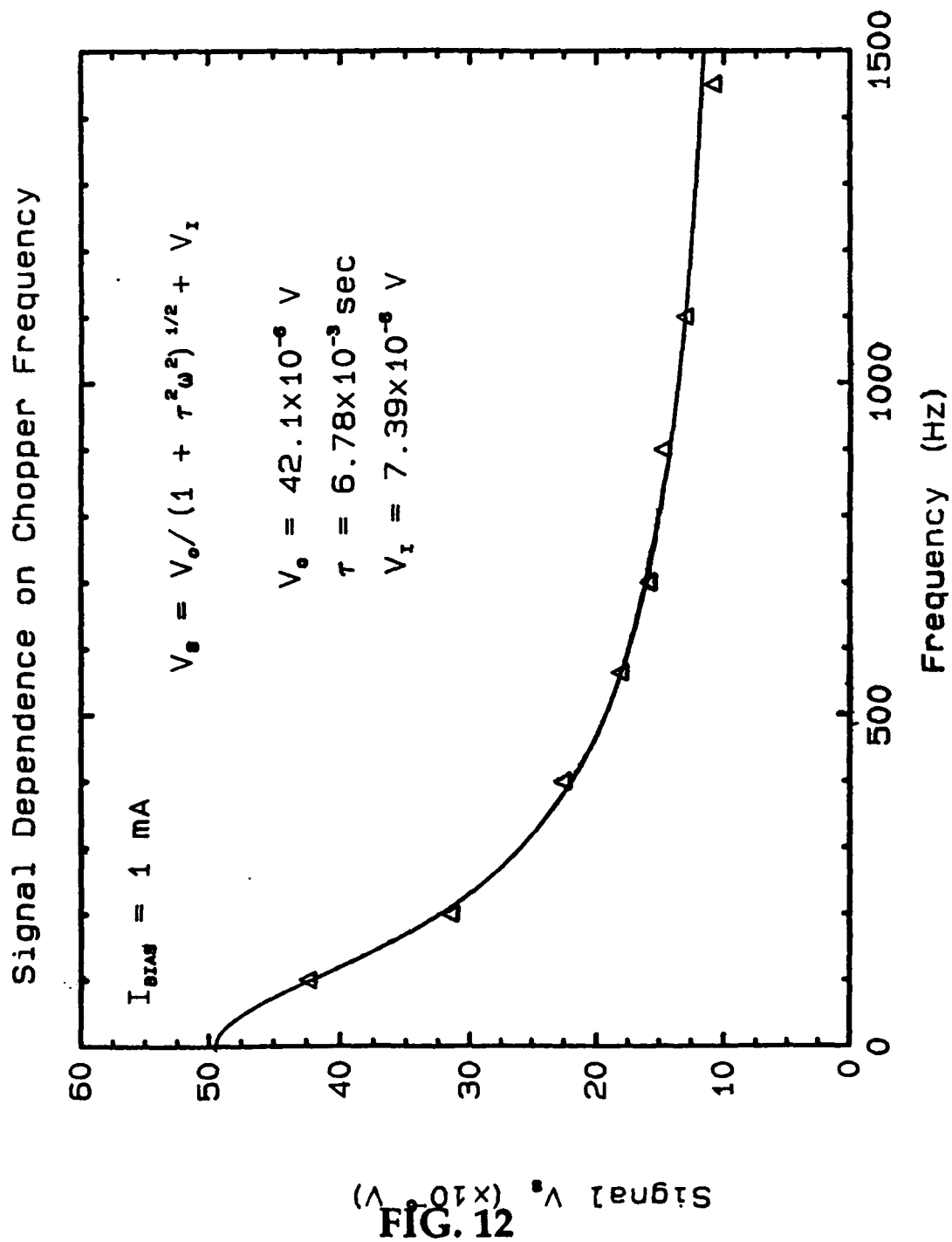


FIG. 11



$$V_s = I \frac{dR}{dT} \frac{P}{K(1 + \omega^2 \tau^2)}$$

• BOLOMETRIC

• $V_s \rightarrow V_I$

$\omega \rightarrow \infty$

temperature side of the signal curve. 3) Finally there is a small temperature offset towards smaller temperature of the signal curve. This offset comes from a small temperature difference between the temperature sensor and the sample under study in the presence of the IR radiation.

The fact that both curves track each other through out most of their temperature span, indicates that there is a bolometric response in our 123 films. However, there is a small shoulder in the low temperature side of the dV/dT vs. T curve that we interpret as a intrinsic component of the signal. Similar type of behavior was interpreted in the low temperature superconductors to be due to an intrinsic response. The maximum of the shoulder happens around 50K. To show further evidence of this intrinsic response we performed a frequency dependent study of the response signal at a temperature of 50K. A purely bolometric signal would have a vanishingly small signal as the frequency was increased beyond the characteristic frequency. Results of this study are shown in Fig. 12. As can be seen from Fig. 12, the signal does not vanish at high frequencies. The signal drops as the frequency increases but stabilizes at high frequencies to a value 7.4 micro volts. This value is comparable with the difference of between the dV/dI vs. T curve (which has the bolometric and intrinsic responses of the sensor) and the dR/dT vs. T curve (which only reflects the bolometric component). The data in Fig. 12 was fitted to a purely bolometric signal plus a frequency independent constant to accounts for the intrinsic component. The good fit corroborates the fact that there is a strong bolometric and intrinsic component in the measured signal. From the fit, one can obtains a characteristic time constant of 6.3 ms for the bolometric signal. This long time constant is characteristic of bolometric responses.

Figure 13 shows a superimposed plot of the voltage noise level together with a plot of the resistance of the film multiplied by the temperature. Both curves track each other relatively closely. This would indicate a Johnson type noise if it was not for the fact that the magnitudes of both curves are not related by the Johnson formula $VJ^2 = 4KTRB$, where VJ is the voltage noise, K is Boltzman constant, T the temperature, R the resistance of the film and B is the band width. From the responsivity of the device and the voltage noise of the device shown in Fig. 14, one can calculate the noise equivalent power of the device as a function of temperature, as shown in figure 15.

In conclusion preliminary research for this project has shown that the fabrication of infra-red bolometric detectors from superconducting thick films is indeed possible. At present these devices do not compare favorably with solid state devices in terms of sensitivity, but ease of fabrication, together with the absence of a requirement for sophisticated manufacturing machinery and techniques may well make thick film detectors a desirable commodity. More research is necessary before conclusive statements as to the presence of an intrinsic response can be made.

1. Y. Enomoto, T. Murakami, J. Appl. Phys. 59, 3807, (1986).

2). Current Injected Superconducting Magnetic Sensors.

It has been previously shown that the nonlinear response of high temperature superconductors to alternating magnetic fields can be employed for detection of weak dc fields in the nanotesla range¹⁻³. In these low density ceramic materials, the generation of circulating currents is not sufficient to prevent the penetration of applied magnetic fields into the bulk of the material. Even fields substantially lower than 1 Oe can easily penetrate between superconducting grains along the grain boundaries. In the case of alternating applied fields, the flux lines sweep in and out of the material lagging the driving field. Low intensity, nanotesla range quasi-dc fields (0.1-1Hz) superimposed on this higher frequency carrier can be detected and measured. Such a detector manufactured using thick film techniques would incorporate an inexpensive fabrication method producing large quantities of sensors with a robust easily packaged device capable of detection and accuracy in the nanotesla field range.

With the philosophy of ease of fabrication and use, a thick film magnetometer has been produced that does not rely on an applied ac magnetic field but rather on an internally produced field driven by a current directly injected into the device (see Fig.16). A 50 μm thick film disc is screen printed onto a ZrO_2 substrate and sintered at 980 C for 8 hours. Electron micrographs reveal average grain size of 5 μm . Electrical connections are provided by two similarly printed 1 $\mu\Omega$ silver tabs. A 200 turn copper wire coil placed against the surface of the device allows for signal detection via the induced voltage of the resultant magnetic field. This voltage is detected by a lockin amplifier with the output being on-line Fourier transformed with a spectrum analyser. A schematic representation of the circuit is shown in Fig. 17. Calibration of the device is enabled by positioning it within the central field space of a Helmholtz coil pair producing a known low intensity, low frequency field perpendicular to the surface of the sensor. This field simulates the dc background to be detected.

Assuming a sinusoidal excitation field $H_{ac}\sin\omega t$, the components of the voltage developed across the detection coil are

$$V_n = \omega AN \{a_n \sin(n\omega t) + b_n \cos(n\omega t)\}$$

where N is the number of turns in the detection coil and A the effective area. a_n and b_n depend on the relation between the ac and dc fields and sensor parameters. As shown in Fig. 18 a the detected signal amplitude shows perfect linearity with applied quasi dc field for fields $10^{-3} < H < 0.5$ Oe and a driving field of 50 KHz. While the sensitivity of the device is currently lower by an order of magnitude than that of devices based on bulk materials, this is more than compensated by an increase in sensitivity to the orientation of the magnetic field. The dimensions are such that sensitivity could also be much improved by stacking a number of such devices in

$$\bullet \text{NEP}$$

$$P_N = \frac{V_N}{R}$$

$$V_N = \langle (V_{\text{MAX}} - \langle V \rangle)^2 \rangle^{1/2} \quad (\times 10^{-6} \text{V})$$

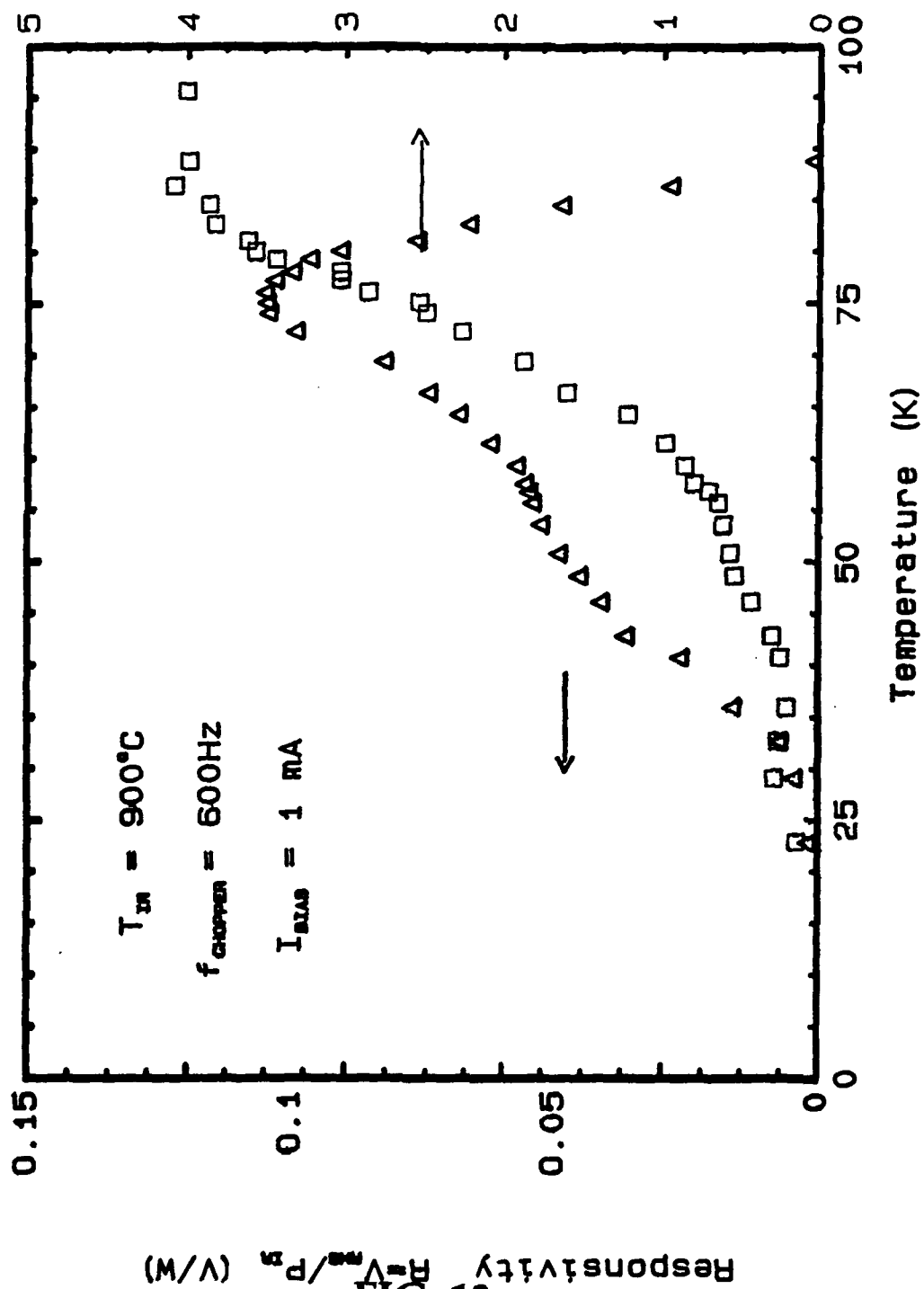


FIG. 13

Temperature Dependence of the Noise Equivalent Power

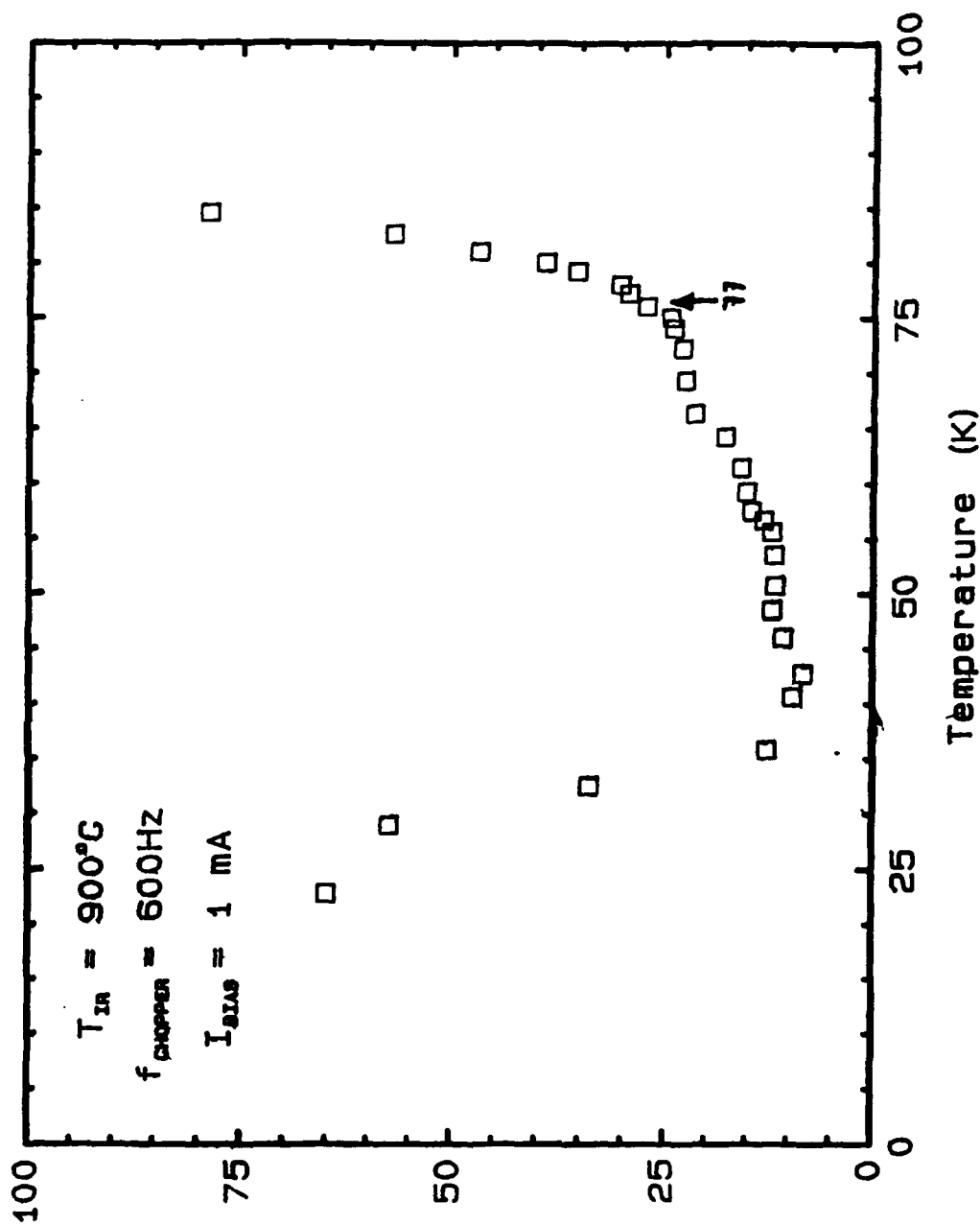


FIG. 14

$$P_N(77) = 25 \mu W$$

$$P_N \gg P_{gear}$$

$$V_J^2 = 4kTRB$$

$$V_N^2 \propto R \cdot T$$

$$V_N \gg V_J$$

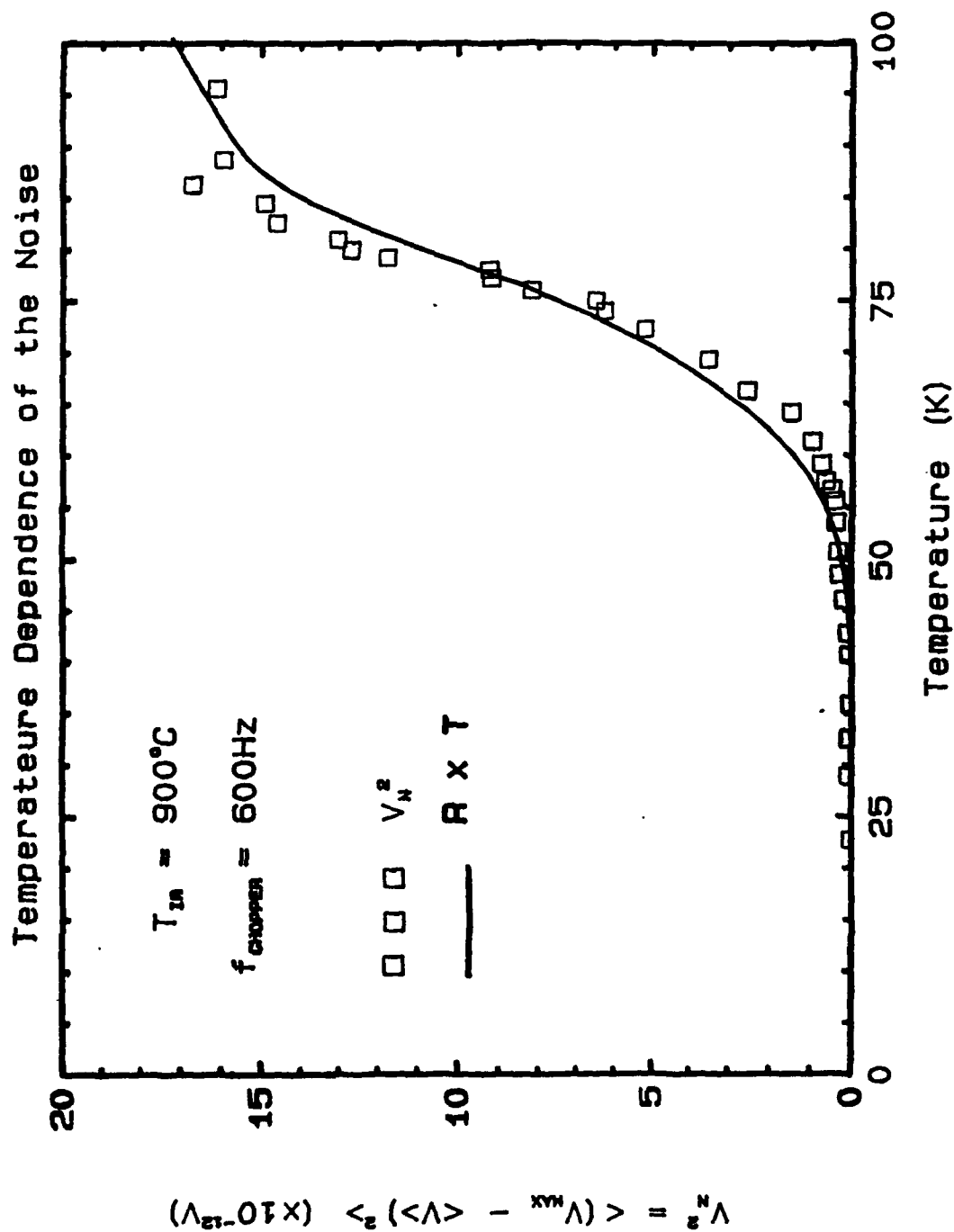


FIG. 15

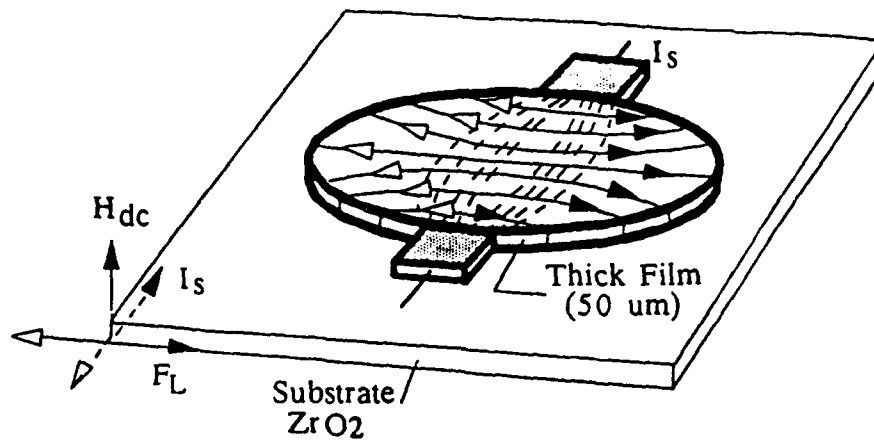


FIG. 16

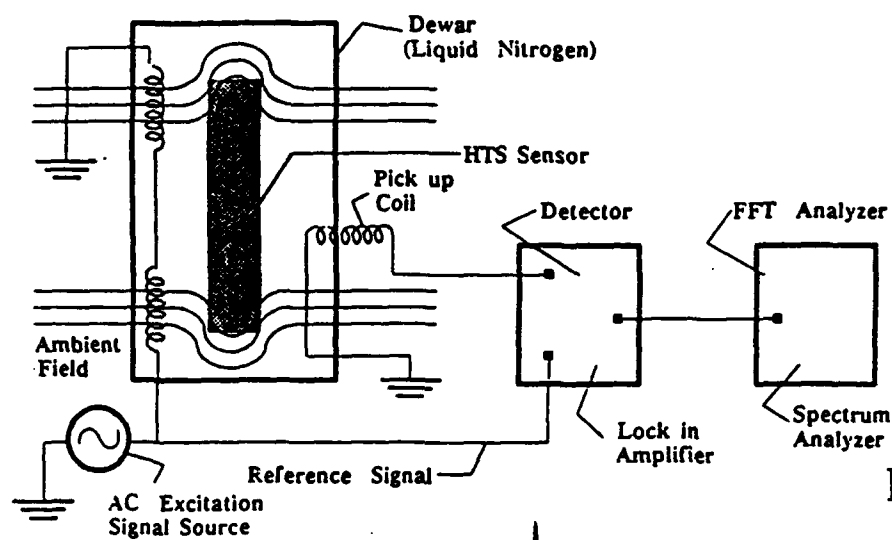


FIG. 17

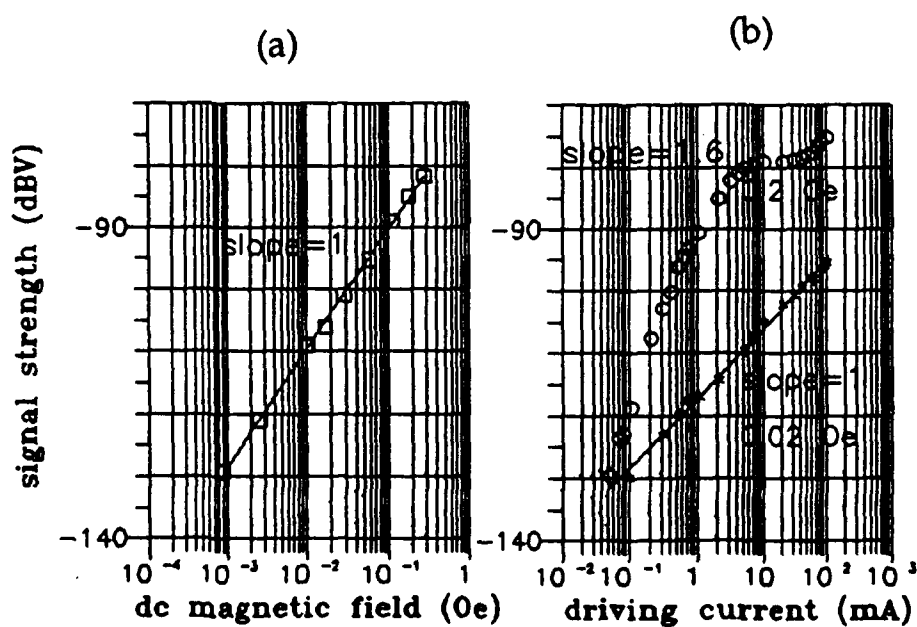


FIG. 18

series. The influence of the ac field is shown in Fig.18 b. For low fields ≤ 0.02 Oe, one observes linear dependence between signal and driving current. At higher fields however, a saturation effect is observed for large values of driving current. Signal amplitude also increases linearly with driving frequency and results with bulk sensors of this type have shown that increases in frequency can have significant impact on device performance.

Studies of the effect of different sintering programs on sensitivity were performed with the expectation that the quality of the intergranular junctions would have substantial effect on device properties. While sintering temperature did not have any effect on sensitivity, increased sintering time leading to larger grain size ($35\mu\text{m}$) gave an improved detector performance.

With the successful testing of a device capable of measuring magnetic fields of order 10^{-9}T and better, the possibilities of fabricating related devices using similar techniques arise. Plans for a magnetic field gradiometer have been discussed, this consisting of a number of simple magnetometers of the type mentioned above stacked and interconnected. Thick film technology would allow these to be produced cheaply in small packages for a wide range of uses.

Suggestions have been made recently that these magnetometers would also be suitable for use in accelerometers, detecting the change in the local magnetic field due to the movement of a magnetic membrane caused by a change in acceleration. Similar devices using SQUIDS as the magnetic monitoring system have been used in gravity wave detectors. Dr. P. Giellisse has received inquiries from the US Army about the possibilities of such a system and has expressed interest in a continued cooperation.

C) Superconducting tapes and wire composites

A general requirement of technological applications of superconducting ceramics in the field of magnet development is that of a ductile wire or tape that can be formed into coils. Because the physical nature of the high temperature superconductors (ie. hard and brittle) is such that this is unlikely to be possible when the material is actually in the superconducting phase, much of the work done in this field is directed towards producing a malleable tape or tube containing the precursors which can then be fired and reacted into the superconducting phase after winding. With much of the resources of this project being orientated towards thick film development, efforts were made to produce a flexible thick film tape that would fit these requirements.

Experiments with two types of superconductor laminated organic tapes ie. superconducting thick films on flexible tapes such as nitrocellulose were attempted. The first of these consisted of a thick layer of superconductor (source being commercial Rhone-Poulenc powder) that could remain free standing after the

organic tape had been burnt away. The second tape was produced as a so-called 'transfer' tape, the original idea being that a pattern of superconductor printed on the tape could be applied to a more solid substrate and bonded into position during the firing process. In their initial unfired state both tapes showed good physical flexibility and durability. The transfer tapes could be bonded to surfaces such as alumina, MgO and stainless steel without difficulty. On firing and consequent burnout of the organic material, the transfer tapes did not show good adhesion to MgO or alumina and, like the thicker tapes, uneven shrinkage of the material during heating due to local variations in the powder density caused the tape to bend, crack and break. Multiple laminations of the material eliminated this problem and after firing at 930 C, samples were found to contain at least 95% 123 phase. The critical temperature of this material was found to be 92 K and J_c 's of 3 A/cm² at 77 K and 40 A/cm² at 2K. While these values are low in comparison with conventional thick films, this method of applying patterns to unconventional substrates has great promise in such fields as electronic connects and microwave cavities.

While the majority of work performed on this contract involved the preparation of thick film structures using 123, studies of the Bismuth based ceramics was also performed. These materials $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (2212) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (2223) have a glassy micaceous structure and as such are more flexible and thus suitable for the formation of wires or self supported structures. Initial studies with thick films of this material using alumina substrates showed strong substrate interaction increasing with furnace time. Samples did show evidence of resistive transitions at 110 K and 80 K but retained a finite resistance down to 10 K.

D) Microwave Cavities and Devices.

One of the major concerns with the application of high temperature superconductors to microwave research is the technological problem with coating large irregularly shaped surfaces with the superconducting ceramic material. While indications from this and other sources reveal that thick films superconductors will likely never obtain the magnitude of critical current found in single crystal thin films such as those produced by laser deposition, the much less complicated preparation methods of the former make it more likely that the first such practical applications will be with polycrystalline thick films. Studies of the surface impedance of typical screen printed thick films were made in collaboration with Dr. D.W. Cooke at Los Alamos National Laboratory. Measurements were performed on a variety of thick film samples with the 22 GHz Cu cavity using the end wall configuration described in the reference below¹. A summary of the data obtained is given in table 1, indicating both the magnitude of typical data and the degree of spread between measurements on different films.

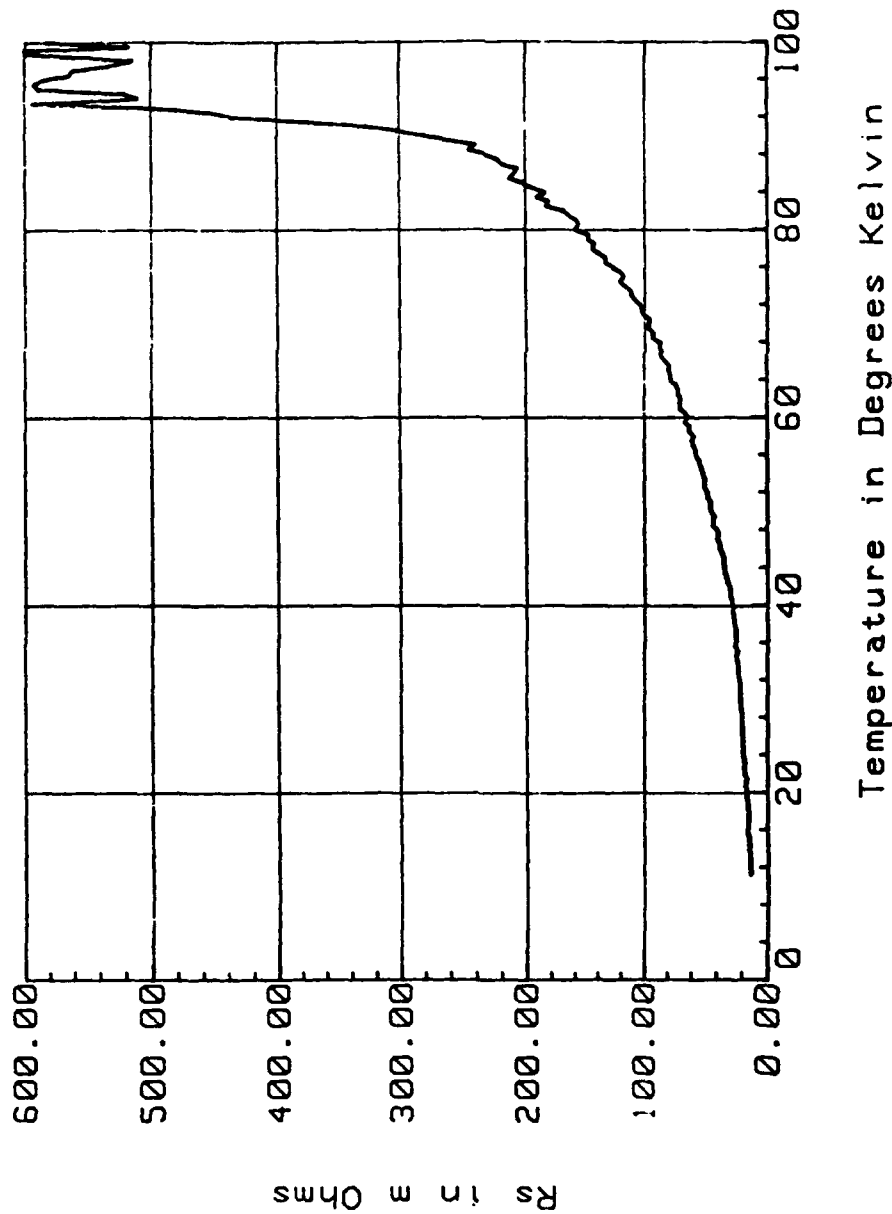
Sample	R_s at 77K in $m\Omega$	R_s at 20K in $m\Omega$
1	982	120
2	656	52
3	677	47
4	136	14
5	550	85
5	700	128
tape cast	133	15
copper	22	11
laser ablated and off axis sputtered films	0.3	-

As can be seen, one of the films and the tape cast material (described elsewhere in this report) gave results comparable to high purity copper. Fig. 19 and 20 show a sample plots of the surface impedance and unloaded Q factor of the cavity respectively.

It is important to note that the critical parameter affecting the measurement of the surface impedance is the quality of the material within a penetration depth of the surface. From studies of the degradation of the electrical properties of the material with exposure to ambient air, it is likely that with greater consideration to protection from the environment, the value of R_s for the 123 samples could be considerably improved. These investigations show that the construction of high temperature superconducting ceramic microwave cavities are a real possibility for the first commercial use of these materials.

- 1) D.W. Cooke et al. Appl. Phys. Lett. 55 914 (1989).

22 11 5QC
22GHZ CAV - JACKCROW TC #1 QC

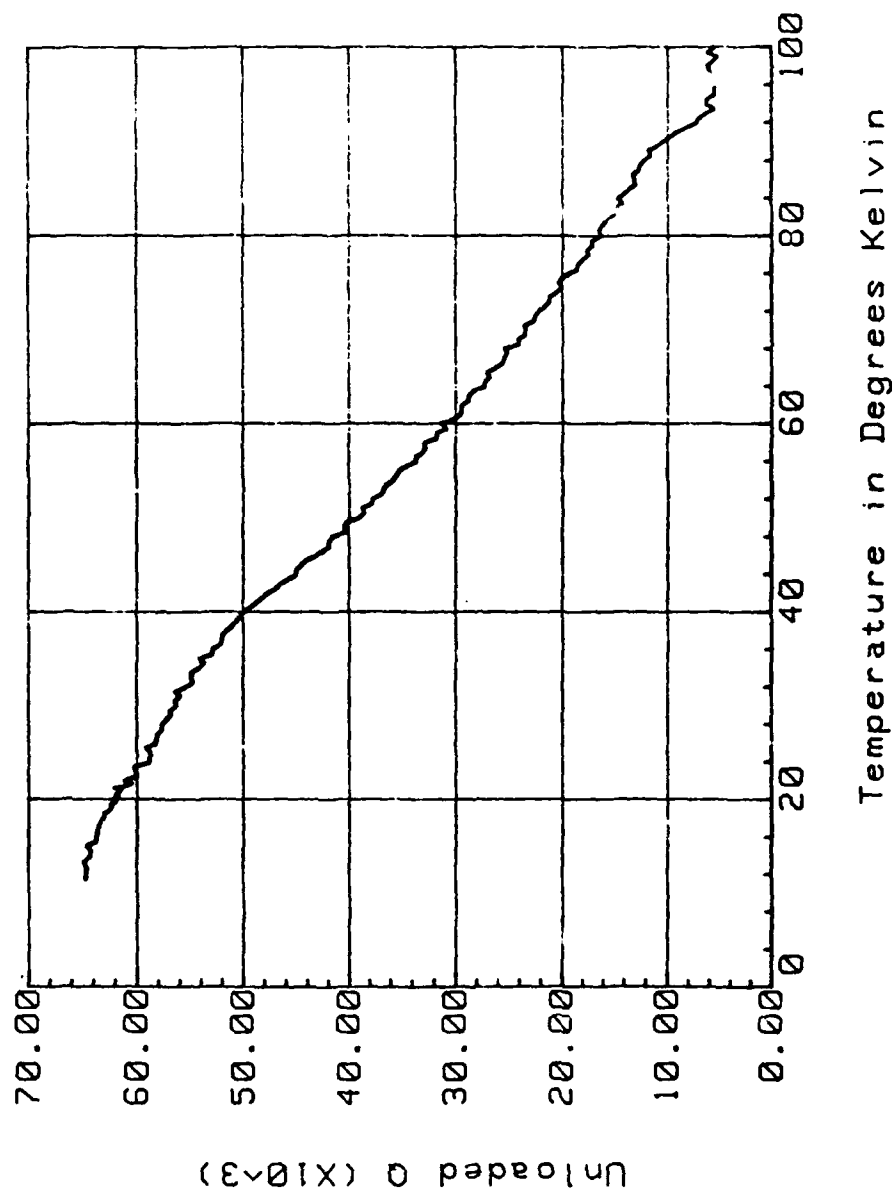


TEMP.
19.7
76.5

VERT. DATA
15.9169
133.6882

FIG. 19

22 11 50C
22GHZ CAV - JACKCROW TC #1 QC



TEMP.
19.5
76.5

VERT. DATA
62.3091
18.4660

FIG. 20

IV) Publications and Presentations.

- 1) Thick Film $\text{YBa}_2\text{Cu}_3\text{O}_7$ Superconductors for Microelectronics Applications. N.L. Corah Jr, R.L. Wahlers, S.J. Stein, I. Perez, J. Schwegler, G.H. Myer and J.E. Crow. Proc. Int. Symp. Microelectronics. ISHM Baltimore (1989).
- 2) Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ Precursors from a fused Eutectic of Sodium and Potassium Hydroxides. N. Coppa, D.H. Nichols, J.W. Schwegler, J.E. Crow, G.H. Myer and R.E. Salomon. J.Mat.Res 4 1307 (1989)
- 3) Specific Heat and Magnetic Susceptibility of the high Temperature Superconductor $(\text{Bi,Pb,Sb})_2\text{Sr}_2\text{CaCu}_2\text{O}_{10}$ Y.Gao, J.E. Crow, G.H. Myer, P. Schlottmann, J. Schwegler and N.D. Spencer. Physica C165 340 (1990).
- 4) Preparation, Thermal Processing Behaviour and Characterization of Powdered and Bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ from Freeze Dried Nitrate Solutions. N. Coppa, J.W. Schwegler, R.E. Salomon, G.H. Myer, A. Bura and J.E. Crow. Submitted to Journal of Materials Research. (1990).
- 5) Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ using Barium Hydroxide Flux. N. Coppa, A. Kebede, J.W. Schwegler I. Perez, R.E. Salomon, G.H. Myer and J.E. Crow J.Mater.Res 5 2755 (1990).
- 6) Superconducting and Magnetic Phase Boundaries in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{M}_x\text{Cu}_2\text{O}_{10}$ with $\text{M}=\text{Y}$ and Pr . Y. Gao, P. Pernambuco-Wise, J.E. Crow, J. O'Reilly, N.D. Spencer, H. Chen and R.E. Salomon. Submitted to Phys.Rev. B (1991).
- 7) Current Injected Thick Film HTS Magnetic Sensors. P.J. Gielisse, H. Nicelescu, B. Roy, P. Pernambuco-Wise, J.E. Crow, G. Sykora and R. Wahlers. Accepted for publication J. Appl. Phys. (1991).
- 8) Effect of Zn Substitutions in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Phases on Reactivity during the Ammoxidation of Toluene. J.C. Otamiri, A. Andersson, S.L.T. Anderson, J.E. Crow and Y. Gao J. Chem. Soc. Faraday Trans. 87 1265 (1991)
- 9) Oxidation of Carbon Monoxide over Cobalt and Aluminum substituted Y-Ba-Cu-O Perovskites. J. C. Otamiri, S.L.T. Andersson and J.E. Crow. (Accepted for publication)

- 10) Synthesis and Characterization of High Transition Temperature Superconductors. Nicholas V. Coppa. Dissertation for the award of Ph.D. degree, Temple University 1990.
- 11) Thermodynamic and Impurity Studies of Bi-Based High T_c Superconductors. Ye Gao. Dissertation for the award of Ph.D. degree, Temple University 1991.
- 12) Synthesis and Characterization of Cupate Superconductors. Richard W. Schaeffer, Dissertation for the award of Ph.D. degree, Temple University (1992).

Presentations.

- 1) Thick Film Processing.
Presented at 3rd Annual International Superconductor Applications Convention, Long Beach CA (1990).
- 2) Thick Film Processing and Thick film Bolometers.
Presented at the first Annual DARPA High Temperature Superconductor Workshop, Santa Barbara, CA. (1989).
- 3) Thick Film Substrate Interaction.
Presented at the first Annual DARPA High Temperature Superconductor Workshop, Santa Barbara, CA. (1989).
- 4) $YBa_2Cu_3O_7$: Thermal Decomposition of Aqueous and Ammonia Solutions of Nitrates and Acetates.
- 5) Preparation, Thermal Processing Behaviour and Characterization of bulk $YBa_2Cu_3O_{7-x}$ from Freeze dried Nitrate Solutions.
Presented at the 1990 MRS Spring Meeting, San Francisco, CA.
- 6) Ten Minute Preparation of $YBa_2Cu_3O_7$ using Barium Hydroxide.
Presented at the 1990 MRS Spring Meeting, San Francisco, CA.
- 7) Superconducting and Magnetic Phase Boundary of $(Bi,Pr)_2Sr_2Ca_{1-x}Y_xCu_2O_8$.
Presented at the 1991 APS March Meeting, Cincinnati, Ohio.
- 8) Specific Heat and Magnetic Susceptibility of (2212) and (2223) Bi-Sr-Ca-Cu-oxide Superconductors.
Presented at the 1991 APS March Meeting. Cincinnati, Ohio.
- 9) Production of High T_c Superconductor Powders by Freeze Drying.

Presented to Second Annual DARPA High Temperature Superconductor Workshop, Boston, MA.

- 8) Xerogels as a Route to Ceramic Oxide Superconductors.
Presented to Second Annual DARPA High Temperature Superconductor Workshop, Boston, MA.
- 9) Thick Film Superconductors: An Overview and Applications.
Presented to Second Annual DARPA High Temperature Superconductor Workshop,
- 10) Transport Properties of Thick Film Superconductors on Yttria Stabilized Zirconia Substrates.
Presented at the 1990 Conference on Magnetism and Magnetic Materials, Boston MA.

V) Principal Participants and their Status

Co-Principal Investigators:

Dr. Jack E. Crow
Director
National High Field Magnet Laboratory
1800 E. Paul Dirac Drive, B223
Florida State University
Tallahassee FL 32306

Dr. Sidney Stein
CEO
Electro-Science Laboratory Inc.
P.O. Box 1059
416E Church Road
King of Prussia PA 19406

Dr. Richard Wahlers
Manager of Product Development
Electro-Science Laboratory Inc.
P.O. Box 1059
416E Church Road
King of Prussia PA 19406

Post-Doctoral Scientists:

Dr. Ignacio Perez
Naval Air Development Center
Warminster
PA 18974
Support provided by DARPA and Temple University

Dr. Paul Pernambuco-Wise
MARTECH
Keen Building
Florida State University
Tallahassee, FL 32306
Support provided by DARPA and Center for Materials Science and Technology, FSU

Technical Support Staff:

Mr. James O'Reilly
MARTECH
Keen Building
Florida State University
Tallahassee, FL 32306

Support provided by DARPA and Center for Materials Science and Technology, FSU

Graduate Student researchers:

D. Nichols
Support provided by DARPA and Temple University

Y. Gao
A. Kebede
G. Cao
S.T. Ting
N. Coppa
R>W. Schaeffer

Support provided by Temple University and/or Center for Materials Research and Technology, FSU

Thick Film Processing and Thick Film Bolometers

N. L. Corah, Jr., S. J. Stein and R. L. Wahlers

Electro-Science Laboratories, Inc., 416 E Church Rd.,
King of Prussia, PA 19406

J. Weaver

General Electric Co., Astrospace Division, P.O. Box 8555,
Philadelphia, PA 19101

I. Perez, J. Schwegler, G. H. Myer and J. E. Crow

Center for Materials Research, Temple University,
Philadelphia, PA 19122

Thick films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been prepared on a variety of polycrystalline substrates including Al_2O_3 , MgO , SrTiO_3 , and Y-stabilized ZrO_2 and the effects of heat treating have been studied. Sharp transitions with $T_c \approx 90\text{K}$ have been obtained on MgO and Y-stabilized ZrO_2 using standard thick film processing techniques. These films have been tested for use as bolometric sensors for broad band infrared radiation. The responsivity has been measured for a variety of thick films and as a function of temperature and chopper frequency used to interrupt the infrared radiation. In addition, attempts to observe an intrinsic Josephson response at $T < T_c$ have been unsuccessful. The effects of thermal processing on the normal and superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ thick films will be presented along with infrared responsivities.

YBa₂Cu₃O₇: Thermal Decomposition of Aqueous and Ammonia Solutions of Nitrates and Acetates

N. Coppa, R. Schaeffer, A. J. Bura, J. Schwegler, J. E. Crow, G. H. Myer and R. E. Salomon

Center for Materials Research, Temple University,
Philadelphia, PA 19122

Superconducting powders of YBa₂Cu₃O_{7- δ} have been prepared by the thermal decomposition of aqueous and ammonia solutions of nitrate and acetate precursors. The aqueous solutions were ultrasonically dispersed in liquid nitrogen and the resulting particles are freeze dried to produce homogeneous fine powders which are mixed at the atomic level. The effects of thermal processing of the freeze dried powders have been studied. Initial care is required to prevent apparent melting due to the redissolving of the nitrates in the water of hydration released during this final stage. The decomposition has been studied using thermal gravimetric analysis and differential thermal calorimetry along with measurements of the room temperature lattice parameters and temperature dependences of the magnetization. In addition to this effort, superconducting YBa₂Cu₃O_{7- δ} has been produced by the thermal decomposition of ammonia solutions of stoichiometric quantities of nitrates and acetates. These solutions are sprayed into a heated zone to produce superconducting powders. The results of these studies will be presented and discussed.

Better Ceramics Through Chemistry IV

Coppa, J. W. Schwegler, R. E. Salomon, G. H. Myer, Center for Materials Research, Temple University, Philadelphia, PA; A. Bura, J. E. Crow, MARTECH, Florida State University, Tallahassee, FL.

Solutions of Y, Ba and Cu nitrate were spray-frozen. Very small particles consisting of atomic mixtures of these salts remained after the water was sublimed. These YBCO precursors were characterized and their behavior was studied in detail while they were thermally decomposed by a variety of techniques. Kilogram size batches are routine. The final YBCO products were obtained as powders and sintered bars. Sintered materials exhibited excellent phase purity (>99%) and super-conducting characteristics ($T_c = 92$ K), while powdered materials had secondary phases present. Some of these samples having high percentages of second phases exhibited sudden drops in resistivity to a few micro-ohms at 200 or 240 K followed by a zero resistance transition at 92 K. Coincident with this drop in resistance was a discontinuity in the magnetization.

Nick 9c
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A
Better Ceramics Through Chemistry IV

TEN MINUTE PREPARATION OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ USING BARIUM HYDROXIDE. N. Coppa, A. Kebede, J. W. Schwegler, I. Perez, R. E. Salomon, G. H. Myer and J. E. Crow, Center for Material Research, Temple University, Philadelphia, PA 19122.

High quality bulk $\text{YBa}_2\text{Cu}_3\text{O}_{x-7}$ was synthesized by fusing stoichiometric amounts of yttrium and copper nitrates and barium hydroxide, in air, using an ordinary bunsen burner. The starting materials go through a short-lived liquid phase yielding a solid black product which was subsequently heat treated, (900 °C, 18-24 hrs, in air, followed by 500 °C, 5 hrs., in O_2). These materials were greater than 99% phase pure with CuO as the only other phase and they exhibited a transition temperature of 92 K, a 15.5% perfect diamagnet response (field cooled), 76% (zero field cooled). This synthesis represents an improvement over the much more labor and time intensive conventional methods in that it allows high quality materials of various compositions to be prepared quickly. A series of praseodymium substituted samples were prepared and their characteristics indicate that Pr homogeneously substitutes at the Y site consistent with earlier works.

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1001 North 17th Street
Westerville, OH 43081

Abstract Submitted for the March
1990 Meeting of the American Physical Society

Sorting Category 25e

Superconducting and Magnetic Phase
Boundary of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ J.E.CROW,
Florida State U; Y.GAO, J.SCHWEGLER and
G.H.MYER, Temple U; N.D.SPENCER, W.R.Grace &
Co.Conn.--The temperature dependence of the
specific heat $C(T)$ for $1.5 \leq T \leq 150\text{K}$ and magnetic
susceptibility $\chi(T)$ for $1.8 \leq T \leq 400\text{K}$ have been
measured on single phase $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$
with $0 \leq x \leq 1.0$. Y^{3+} substitutes for Cu^{2+} and
drives the superconducting transition
temperature T_c to zero for $x \approx 0.7$. For $x > 0.7$,
the temperature dependence of the electrical
resistivity is semiconductor-like and the Cu-
ions magnetically order. $C(T)$ as $T \rightarrow 0$ can be
fit to $\gamma T + \beta T^3$ with γ slowly increasing with x ,
reaching 13 mJ/mol K^2 for $x = 1.0$. These results
will be presented and discussed.

+Work supported by DARPA/ONR Contract
No.N00014-88-0587.

Signature of APS Member

Jack E.Crow
Keen Bldg, Rm411
Florida State University
Tallahassee, FL 32306

R.P.Guertin/Tufts U.
Suggested Chairperson

Abstract Submitted for the March
1990 Meeting of the American Physical Society

Sorting Category 25a

Specific Heat and Magnetic Susceptibility of (2212) and (2223) Bi-Sr-Ca-Cu-Oxide Superconductors." Y.GAO, G.H.MYER, P.SCHLOTTMANN and J.SCHWEGLER, Temple U; J.E.CROW, Florida State U.; N.D.SPENCER, W.R.Grace & Co.-Conn.--The temperature dependence of the specific heat $C(T)$ for $1.5 < T < 150K$ and the magnetic susceptibility $\chi(T)$ for $1.8 < T < 400K$ of single phase $(Bi,Pb,Sb)_2Sr_2Ca_2Cu_3O_{10}$ and $(Bi,Pb)_{.2}Sr_2Ca_1Cu_2O_8$ has been measured. A well-defined anomaly in $C(T)$ in the vicinity of the superconducting transition temperature T_c is observed. Approximating this anomaly by a discontinuity in $C(T)$ at T_c which conserves the entropy change near T_c leads to $\Delta C = 6.2 \pm 0.2$ J/mol K and $T_c = 109K$ for the 2223 phase and $\Delta C = 2.4 \pm 0.3$ J/mol K and $T_c = 81K$ for the 2212 phase. Using the temperature independent contribution to $\chi(T)$ to estimate γ , ΔC is close to the weak coupling BCS value and the electrons with the CuO_2 -planes are highly correlated with band mass $\approx 10m_0$ for both phases. These results along with measurements of $C(T)$ as $T \rightarrow 0$ will be presented and discussed.

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Signature of APS Member

Jack E.Crow
Keen Bldg, Rm411
Florida State University
Tallahassee, FL 32306

D.Finnemore/TSU
D.M.Ginsberg/U.ILL
Suggested Chairpersons

Abstact Submitted to
Second Annual DARPA High Temperature
Superconductivity Workshop
October 3-5,1990

Session: V-B

**Production of High T_c Superconductor Powders by
Freeze Drying**

N. Coppa, G. Myer, R. E. Salomon and J. E. Crow*, Center for Materials Research, Temple University, Philadelphia, PA 19122

Stoichiometric mixtures of Y, Ba and Cu nitrates were dissolved in an aqueous solution to give either the 123 or 124 final product. These solutions were ultrasonically dispersed into liquid nitrogen, the water was removed from the frozen snow using freeze drying techniques. The final hydrate free product was shown to consist of a random solid solution of the metal ions by both XRD and heat of solution calorimetry. This material was then thermally decomposed and allowed to react to form the final product. The final products were fully characterized by resistivity, magnetic susceptibility, TGA, DSC, XRD and SEM. The special advantages accrued to the preparation of both the 123 and 124 material using this technology will be presented and discussed.

*Present address: Center for Materials Research and Technology, Florida State University, Tallahassee, FL 32306

Abstract Submitted to
Second Annual DARPA High Temperature
Superconductivity Workshop
October 3-5, 1990

Session: V-B

**Xerogels as a Route to Ceramic Oxide
Superconductors**

Jorge Macho, G. Myer, J. E. Crow* and R. E.
Salomon, Center for Materials Research, Temple
University, Philadelphia, PA 19122

Single phase $\text{YBa}_2\text{Cu}_3\text{O}_7$ powders have been obtained by a new method of precursor preparations. Y, Ba and Cu salts were dissolved in water and gelled using an organic gelling agent. The gel was dried and ground to obtain the xerogel precursor which is stable even under high humidity conditions. Several organic gelling agents have been tested with gelatin leading to the best results. The xerogel precursor was analyzed using X-ray diffraction and the results are consistent with an atomic mixture of the three metals without any phase separation. The optimal heat treatment of these xerogel precursors have been established using TGA and XRD along with measurements of the temperature dependence of the resistivity and magnetic susceptibility. The temperature dependence of the resistivity is linear above $T_c = 92\text{K}$ and extrapolates to zero for $T=0\text{K}$. Scanning electron microscope studies of the powders shown a particle size less than 1 micron.

*Present address: Center for Materials
Research and Technology, Florida State
University, Tallahassee, FL 32306

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October 3-5, 1990

Session: V-A or VI-A

Thick Film Superconductors: An Overview and Applications

Ignacio Perez, Naval Air Development Center, Warminster, PA; P. Wise and J. E. Crow, Florida State University, Tallahassee, FL; M. Velasques, R. Wahlers and S. Stein, Electro-Science Laboratories, King of Prussia, PA

Thick films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been produced on Y stabilized ZrO_2 (YsZ) using conventional belt processing with peak firing temperatures between 930-1025C. The films have a metallic resistivity above T_c and a sharp transition from the normal to superconducting state in the vicinity of 92K. Critical current densities J_c of $\approx 1000\text{A}/\text{cm}^2$ at 77K have been obtained for films fired at 1010C. J_c values when processing at and below 980C were under $10\text{A}/\text{cm}^2$ at 77K. XRD and microstructure studies have indicated the presence of second phases in the higher temperature processed films which have aided in the sintering and enhancement of current carrying capacity. The temperature dependence of the resistivity and J_c along with XRD and microstructural analysis of these films will be presented. Preliminary results impacting on possible application areas will also be discussed.

TRANSPORT PROPERTIES OF THICK FILM SUPERCONDUCTORS ON YTTRIA STABILIZED ZIRCONIA SUBSTRATES. Ignacio Perez, Naval Air Development Center, Warminster PA; Paul Weiss, Jack E. Crow, Florida State University, Tallahassee FL; Mark Velasquez, Richard Wahlers, Sidney Stein, Electro Science Laboratories, King of Prussia PA.

Thick films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ have been produced on Yttria stabilized zirconia using a conventional belt furnace. The sintering temperatures studied were 930, 980, 1000 and 1010°C. Critical current densities of up to 1000 A/cm² at 77K have been obtained in films fired at 1010°C. X-ray data showed a large number of second phases when processing at this high temperature. Jc values when processing at temperatures at and below 980°C were under 10 A/cm² at 77K. It is inferred that the presence of second phases has aided in the sintering of the grains. Resistivity as a function of temperature, Jc values at 77K, x-ray analysis and microstructural analysis of these films will be presented.

Ignacio M. Perez
Code 6063
Naval Air Development Center
Warminster, PA 18974-5000

Phone: (215) 441-1681
FAX: (215) 441-3739

Thick Film $\text{YBa}_2\text{Cu}_3\text{O}_7$ Superconductors For Microelectronic Applications

N.L. CORAH, JR., R.L. WAHLERS AND S.J. RAFFIN

Electro-Science Laboratories, Inc.

King of Prussia, PA 19406

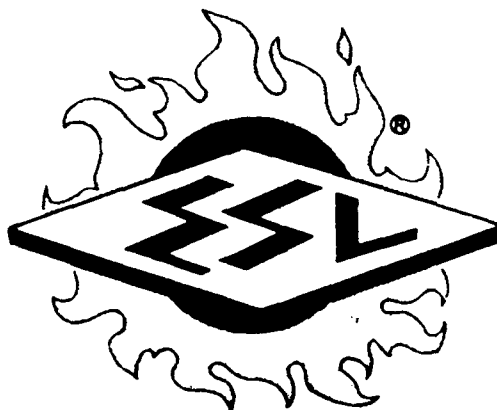
and

I. PEREZ, J. SCHWEGLER, G.H. MYER AND J.E. CROW

Center for Materials Research

Temple University

Philadelphia, PA 19122



ELECTRO-SCIENCE LABORATORIES, INC.

416 East Church Road, King of Prussia, Pennsylvania 19406

Telex 83-4788 • Cable ELECTRO-KOP • Fax 215-272-6759 • Telephone (215) 272-8000

Thick Film $\text{YBa}_2\text{Cu}_3\text{O}_7$ Superconductors For Microelectronic Applications

N.L. CORAH, JR., R.L. WAHLERS AND S.J. STEIN

Electro-Science Laboratories, Inc.

King of Prussia, PA 19406

and

I. PEREZ, J. SCHWEGLER, G.H. MYER AND J.E. CROW

Center for Materials Research

Temple University

Philadelphia, PA 19122

ABSTRACT

The performance of $\text{YBa}_2\text{Cu}_3\text{O}_7$ based thick films were evaluated after firing on a variety of polycrystalline substrates. A high degree of preferred orientation of the superconducting phase was obtained when films were fired at 980°C , especially on 96% alumina. A thick film silver conductor composition, ESL #9990 was employed to form terminations to superconductor films with contact resistances of 10^{-4} - $10^{-2}\Omega\text{-cm}^2$ at 77K.

Keywords: Thick Film, Superconductors, Contact Resistance, Substrate Compatibility

INTRODUCTION

The discovery of oxides with superconducting transition temperatures (T_c) greater than the boiling point of liquid nitrogen (77K)^{1,2} has generated intense research activity throughout the world. Much of this activity has been stimulated by the enormous potential for applications at $T > 77\text{K}$. Since the pioneering discoveries of Bednorz and Muller³, there have been numerous oxide superconductors identified with $T_c > 77\text{K}$ but most of the research has centered on $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) with $T_c \approx 92\text{K}$.

YBCO crystallizes in an orthorhombic structure with Cu-O planes parallel to the basal plane⁴. The superconductivity and free charge carriers primarily reside in these closely coordinated Cu-O planes leading to highly anisotropic normal and superconducting state properties⁵. Both single crystal and thin film studies have indicated that the anisotropy of the superconducting properties is an important factor influencing properties critical to many applications. The requirement for preferred alignment is most dramatically evident in a comparison of critical current densities for bulk processed ceramic samples versus thin films or single crystals. The critical current density, J_c , is the maximum current that may be applied to a unit cross-sectional area without incurring resistive losses. Thin films grown such that their c-axis was perpendicular to the substrate, have exhibited J_c values of $\sim 10^6\text{A/cm}^2$ at 77K⁶. However, for most bulk processed material, J_c has been limited to much lower values, i.e., $J_c \leq 1000\text{A/cm}^2$ at 77K. The higher J_c -values for thin films as compared to bulk ceramics has been attributed to the preferred alignment with the Cu-O planes parallel to the substrate and the stronger intergrain coupling of the superconducting electrons.

Presented in this paper are the results of initial efforts aimed at the development of optimal processing procedures for screen printed superconducting thick films. Such films have numerous potential applications in a variety of areas such as chip-to-chip interconnects, high information density data transmission lines and high current applications, e.g., microwave devices.

To produce high quality thick film superconductors both compatible substrates and normal metal contacts will be required. The literature shows⁷ that YBCO suffers from unfavorable chemical interaction with most substrate materials. This is particularly apparent at the high temperatures that are necessary to achieve the high density and adhesion required for thick films. When making electrical contact to a superconductor it is important to minimize the resistance of the superconductor/normal metal interface. If the contact resistance is too high the heat generated could drive the superconductor into a normal state locally, thus limiting the current carrying capacity of the film.

Superconducting thick films have been fabricated on a variety of polycrystalline substrates, e.g., 96% Al_2O_3 , 99.6 Al_2O_3 , MgO , Y-stabilized ZrO_2 (YSZ) and SrTiO_3 , using standard screen printing methods. The temperature dependence of the electrical resistivity $\rho(T)$ and J_c were measured to characterize the normal and superconducting properties of the thick films. All the thick films studied had resistive transitions to the superconducting state starting at $T_c(\text{onset}) \approx 92\text{-}95\text{K}$ and $T_c(\text{zero})$ values (temperature where $\rho(T) \rightarrow 0$) dependent on the substrate and thermal history. In addition to the transport measurements, the results of x-ray diffraction analysis of the films are reported below.

EXPERIMENTAL

A superconducting thick film paste was prepared by combining pre-reacted YBCO based powders and other select ingredients with an appropriate organic vehicle. Films were screen printed on various substrates using a 200 mesh screen with a 38 μ m thick emulsion. In most cases the substrates were pre-terminated with ESL #8884 Au fired at 980°C.

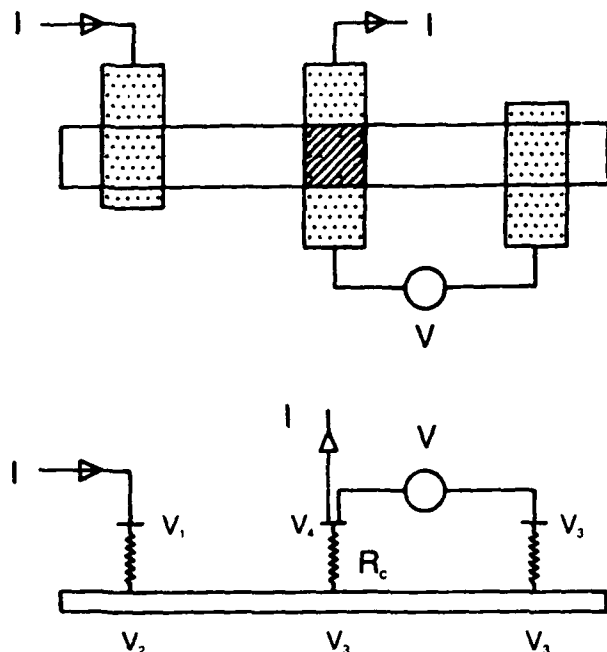


Figure 1 - Diagram of the quasi-four probe contact resistance measurement technique.

All samples were dried at 125°C in a convection oven for 10 minutes before firing. The films were fired at temperatures ranging from 850 to 980°C in air using belt furnaces configured for typical thick film firing cycles. A subsequent oxygen anneal was employed to optimize the superconducting properties. The samples were heated in flowing oxygen to 400-600°C and held at this temperature for 2 hours before cooling at 1°C per minute to room temperature. The fired film thickness was typically 30-50 μ m as measured with a surface profilometer.

The resistivity and transport critical current density were evaluated by four probe dc resistivity measurements. This technique cancels out resistance contributions from the normal metal contacts.

The contact resistance was measured using a quasi-four probe technique. This method allows the resistance of a single contact to be evaluated independent of the resistance of the superconductor film. As illustrated in Figure 1, a current is applied which flows through the contact under test while the voltage drop is measured between two separate sections. Since there is no current flowing through the voltage measuring legs, the voltage drop is primarily due to the resistance of the contact under test.

X-ray diffraction analysis was performed using a Rigaku diffractometer with CuK α radiation. The fired films were mounted and measured in a manner that allowed preferred orientation normal to the substrate surface to be analyzed.

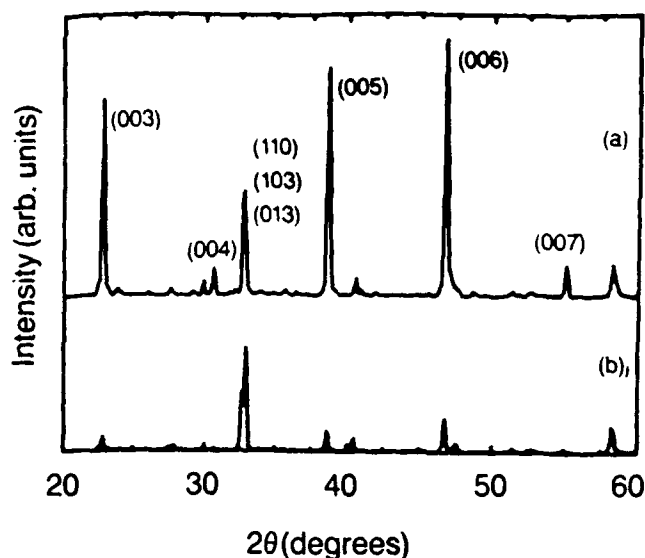


Figure 2 - Ray diffraction patterns of a YBCO thick film fired at 980°C on 96% alumina (curve (a)) and a randomly oriented powder (curve (b)).

RESULTS AND DISCUSSION

Thick Film Structure

Shown in Figure 2 are x-ray diffraction patterns for a YBCO thick film fired at 980°C on a 96% alumina substrate (curve (a)) and a randomly oriented powder sample (curve (b)). X-ray diffraction analysis reveals that a high degree of preferred orientation was achieved when firing samples at 980°C. The very high intensity of the <003>, <005> and <006> reflections indicates that the crystallographic c-axes of most of the YBCO crystals are perpendicular to the substrate surface. This is an ideal situation since the high current carrying copper-oxygen planes are in the a-b crystallographic plane and thus oriented parallel to the substrate and the flow of current. However, the x-ray diffraction pattern also reveals the presence of Y₂BaCuO₅, BaCuO₂, and CuO, the decomposition products of YBCO. The presence of these impurities is deleterious to the superconducting properties.

The 96% alumina substrates yielded the highest degree of crystalline alignment and the largest quantity of impurity phases. All of the other substrates tested showed less preferred orientation and smaller percentages of the undesirable minor phases. The electrical properties of thick film superconductors may be enhanced dramatically by this preferred orientation once the production of non-superconducting phases is controlled.

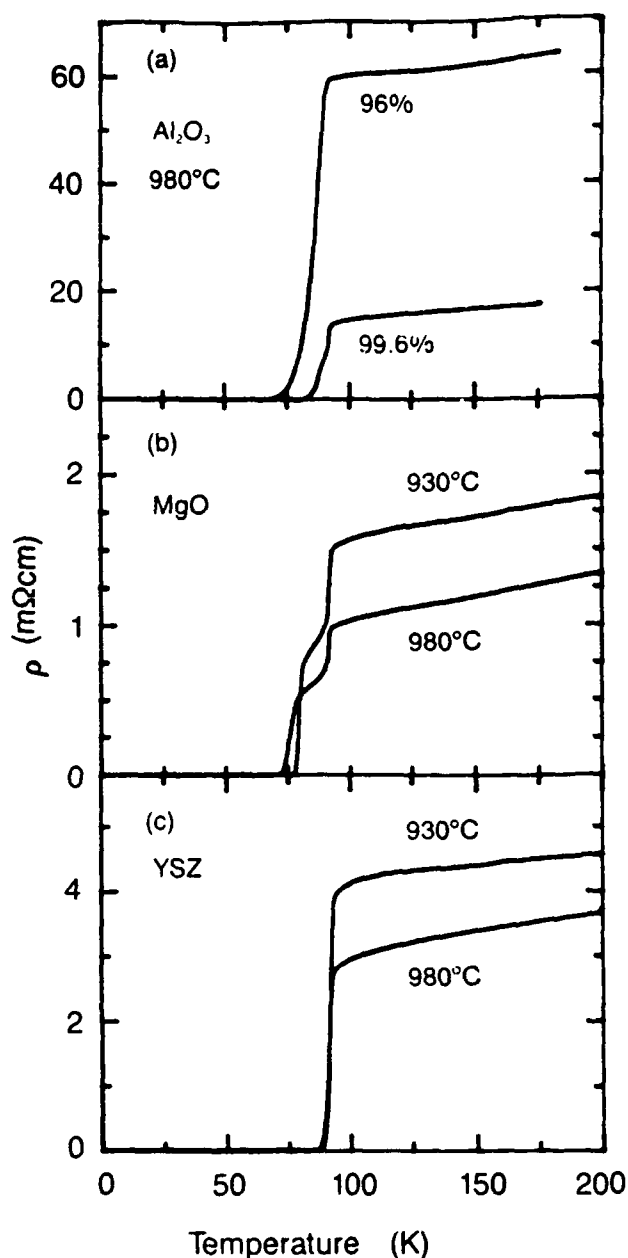


Figure 3 - Resistivity vs. temperature for: a) films fired at 980°C on 96% and 99.6% alumina, b) films fired at 930 and 980°C on MgO and c) films fired at 930 and 980°C on yttria-stabilized zirconia.

Superconductor Properties

The following sections describe the electrical properties of YBCO thick films fired on different polycrystalline substrates. Initial experiments were run at firing temperatures of 850, 930 and 980°C. Adhesion was found to be inadequate for 850°C fired samples so that all subsequent comparison testing was limited to firing temperatures of 930 and 980°C.

Alumina

On 96% alumina the films fired at 980°C typically exhibited a T_c (zero) value around 68K and metallic behavior ($dR/dT > 0$) above T_c (onset). The samples fired at 930°C were generally semiconducting ($dR/dT < 0$) above T_c (onset) and

only became fully superconducting around 54K. Resistivity is plotted as a function of temperature for films fired at 980°C on 96% and 99.6% alumina in Figure 3a. The sample fired on 99.6% alumina exhibits a lower normal state resistivity than the sample on 96% alumina and has a T_c (zero) of 79K as compared to 68K for the 96% alumina sample.

The critical current density of these samples was measured at 4.2K in zero applied magnetic field. The 980°C fired sample on 96% alumina exhibited a J_c of 100 A/cm² as shown in Table I. Lowering the firing temperature to 930°C reduced the J_c to less than 5 A/cm². Firing on 99.6% alumina at 980°C produced a J_c of 5 A/cm².

All of the samples fired on alumina show broad resistive transitions which are indicative of weakly linked superconductors. It has been shown⁷ that aluminum diffuses into YBCO thus contaminating the structure. The presence of this Al contamination along with the previously noted impurity phases may be limiting connectivity in these films.

TABLE I: ZERO RESISTANCE TEMPERATURE AND CRITICAL CURRENT DENSITIES OF FILMS FIRED ON VARIOUS POLYCRYSTALLINE SUBSTRATES

SUBSTRATE	* T_f (°C)	T_c (zero) (K)	J_c (4.2K) (A/cm ²)
96% Al ₂ O ₃	930	54	3
	980	68	90
99.6% Al ₂ O ₃	980	79	5
MgO	930	77	230
	980	72	625
YSZ	930	86	30
	980	86	25
SrTiO ₃	930	48	---
	980	74	---

* T_f = Firing Temperature

Magnesium Oxide

Films fired on polycrystalline MgO typically exhibit higher zero resistance temperatures than those fired on alumina. The T_c (zero)'s are around 77K and 72K for films fired at 930 and 980°C respectively. Typical resistivity curves for films fired on MgO are shown in Figure 3b. All of the films fired on MgO exhibit metallic behavior above the superconducting transition temperature. The transitions show some broadening possibly due to interaction with the substrate material.

Films on MgO yielded the highest critical current densities with the 980°C fired samples exhibiting 600-700A/cm². The films fired at 930°C have higher zero resistance temperatures but lower J_c 's (200-300A/cm²). Figure 4 shows the critical